

# HEAT OF REACTION OF PROCESSING ASPHALT

By

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HEAT OF REACTION OF PROCESSING ASPHALT

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Experimental procedures were developed and experimental equipment was constructed for the purpose of measuring the heat of reaction of asphalt air blowing, catalytic air blowing, and sulphurization.

In the air blowing process, three asphalts of varied composition were studied at two reaction temperatures and three softening point ranges. It was found that the reaction was exothermic with a heat of reaction varying between -61 and -72 kilocalories per gram mole of oxygen reacting depending upon the composition of the asphalt and the reaction temperature, which were shown to be statistically significant factors. The extent of completion of the reaction had no effect on the heat of reaction. Dehydrogenation of naphthenic structures was proposed to be the principal reaction occurring, especially in asphalts with a high naphthenic or paraffinic content.

Polymerization and the formation of oxygen containing groups also contribute to the reaction. The effect of temperature on the heat of reaction was shown to be more pronounced with asphalts having a high aromatic content.

Addition of phosphorus pentoxide to the asphalt proved to have no effect on the heat of reaction, but addition of aluminum chloride decreased the magnitude of the heat of reaction by 9 kilocalories per gram mole of oxygen reacted, a difference that was statistically highly significant. Aluminum chloride was postulated to retard preferentially dehydrogenation reactions in favor of reactions forming oxygen containing groups.

The sulphurization of asphalt was found to be an endothermic reaction with the heat of reaction varying between 8 and 12 kilocalories per gram mole of sulphur reacted depending upon the type of asphalt, which was shown to have a highly significant effect. It was concluded that the naphthenic rings in the asphalt are completely dehydrogenated to aromatics. Polymerization by both sulphur and carbon linkage was indicated.

Both sulphur and oxygen were postulated to dehydrogenate and polymerize asphalt. The primary differences in the two were that oxygen dehydrogenated only one or possibly two bonds of the naphthenic rings, while sulphur dehydrogenated all three bonds and that polymerization is accomplished more by sulphur linkage in the sulphurization process than by oxygen linkage in the air blowing process.

## CHAPTER I

### INTRODUCTION

Asphalt is one of the oldest engineering materials known to man; its earliest recorded use was about 3800 B.C. There are records of the use of asphalt by the Mesopotamians, Babylonians, Assyrians, Greeks, and Romans. The comparatively recent expansion of highways has resulted in the use of asphalt in tremendously large quantities; in 1962 over 200 million tons of asphalt were used in the United States alone. Since 1854, when the first asphalt roadway was laid in Paris, paving products have accounted for most of the asphalt produced. At present 73 per cent of the total production is used in roads and airports. Roofing products account for 17 per cent with the remaining 10 per cent finding application in such miscellaneous products as tiles, floor coverings, paints, insulation, rust preventatives, and bituminized paper products (1).\*

Asphalt is frequently processed chemically to modify its physical properties. The most widely used of these processes is the "air blowing process," which was first patented by E. J. DeSmedt (20) in 1881. DeSmedt found that oxidation of asphalt resulted in a

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\*Underlined numbers in parentheses refer to the List of References at the end of this dissertation.

product which had a greater tenacity and was less brittle and less liable to be affected by air or water. In 1894 F. X. Byerley (15) developed a process for oxidizing asphalt which consisted of blowing air through asphaltic oils maintained at temperatures between 400 and 600 °F. The present practice as reported by Abraham (1) is to blow the asphalt at a temperature of 450 to 575 °F. at a rate of 30 to 50 cubic feet of air per minute per ton of asphalt for a period of 5 to 12 hours. The reaction is carried out industrially either as a batch or continuous process.

A modification of the air blowing process is the production of "catalytic asphalt" in which asphalt is air blown in the presence of a catalyst. The advantage of catalytic asphalts is a modification of the physical properties which is desirable for certain applications. The first patent for such a process was issued in 1899 to J. W. Hayward (40), who recommended the addition of limestone dust in the inlet air. Since then there have been many different catalysts recommended and patented but the ones most widely in use at the present are the metal chlorides, phosphorus pentoxide, and phosphorous sulphides.

A third method of processing asphalt is the treatment of asphalt with sulphur. Although this process antedates the two previously mentioned, being first patented by A. G. Day (19) in 1866, it is no longer used industrially, having been replaced by the air blowing process, which is cheaper and yields a similar product.

In this process, known as the "Dubb's Process" after a subsequent patent holder (22), 20 to 25 per cent sulphur was reacted with asphalt at a temperature of about 600 °F. until the evolution of gas ceased. Although this process has not been used in nearly 50 years, interest in it has been revived because of the work of Ufford and Vlugter (105).

## CHAPTER II

### THEORY

#### A. Asphalt Composition

Asphalt is usually regarded as a complex mixture of high molecular weight hydrocarbons. A more specific statement concerning chemical composition is difficult because the extremely large number of compounds occurring in asphalt make chemical analysis exceedingly complicated. The classification of asphalt as a hydrocarbon is itself fallacious since varying quantities of oxygen, sulphur, and nitrogen are known to be present in asphalt molecules. According to Labout (57) and Kalichevsky and Stagner (51), the oxygen is present in the form of carbonyl, carboxylic, and hydroxyl compounds; nitrogen is present as porphyrins and porphyrin metal complexes; while the sulphur, as well as some of the nitrogen and oxygen, appears in heterocyclic rings. Hempel (41), Sergienko and his coworkers (96), and Abraham (2) have also reported the existence of nickel, vanadium, and traces of other metals in asphalt.

The molecular weight of asphalt molecules has been reported by Pfeiffer and Saal (80) and Marcusson (67) to be in the range of 400 to as high as 100,000. The more recent evidence of Winniford (106), Eckert and Weetman (24), and Griffin, Simpson, and Miles (35) indicates, however, that the upper limit of molecular weight may be no higher than 4,000 or 5,000. The

high values previously reported for the molecular weight of asphaltenes, the highest molecular weight fraction of asphalt, are attributed to the existence of free radicals in the asphaltene molecules which form low energy bonds between several asphaltene molecules. The existence of free radicals in asphalt has been reported by Leybourne and Schweyer (58), Yen, Erdman, and Saraceno (110), Brown, Gutowsky, and Van Holde (12), and Pitchford (81) using different methods.

The structure of the asphalt molecule remains pretty much unknown. Evidence to date indicates that an "average" asphalt molecule consists of a condensed ring structure containing either naphthenic or aromatic rings, or both, with paraffinic side chains attached to the ring. About half the carbon atoms are reported by Murphy (71) to be in aromatic or naphthenic rings, the other half in side chains. The mass spectrometric analysis of asphalt by Clerc and O'Neal (16) indicates that most of the carbon is in aromatic or heterocyclic rings. Ziehmman (112) has found that ring clusters are connected by aliphatic side chains. According to Alexander and Shurden (3), olefin structure is normally present only in asphalts derived from thermal cracking operations.

Labout (57) has stated that the components of asphalt may be considered to contain groups of four basic forms: Saturated aliphatic groups or paraffins, naphthenic groups, aromatic groups, and aliphatic groups with olefinic double bonds. All four basic structures may exist in one asphalt molecule.

## B. Fractionation of Asphalt

Since asphalts from different sources are known to vary in their composition, it is desirable to classify specific asphalts according to their general chemical composition. The literature shows numerous separation procedures which physically separate asphalt into components arbitrarily designated by the individual investigator.

The oldest and one of the most widely accepted classifications is the method developed by Marcusson (63) in 1916, which designates the asphalt components as asphaltenes, resins, and oils. The asphaltenes are the high molecular weight fraction obtained by precipitation methods using non-polar hydrocarbon solvents. The resins are the intermediate molecular weight fraction which is adsorbed on various solid adsorbants. The fraction not retained on the adsorbant is called the oils; it is the lightest portion of the asphalt and similar to lubricating oil.

The asphaltenes are considered to be cyclic in structure, the rings resulting from copolymerization. The rings are reported to be naphthenic as well as aromatic with attached side chains three or four carbon atoms long. Barth (8) reports that the asphaltenes contain the greatest percentage of oxygen, nitrogen, and sulphur. The carbon-hydrogen ratio is reported to be as low as 0.8 and as high as 1.0 by Bestougeff and Bargman (9), Griffin, Simpson, and

Miles (35), Alexanian and Louis (4), and Thurston and Knowles (102) investigating different asphalts.

The asphaltene fraction has been subjected to infra-red analysis by Yen and Erdman (108) and x-ray diffraction by Yen, Erdman, and Pollack (109). Infra-red analysis shows the aromatic clusters to be peri-condensed while the naphthenic clusters are both peri- and kata-condensed. Heat treatment of the asphaltenes results in some kata-condensation of aromatics. The existence of open chain carbonyl groups is verified, and possibly aryl ketones. Many of the aromatic clusters are substituted to a high degree by naphthenic and paraffinic groups. The aliphatic portion of the asphaltene structure was assumed to consist of short, unbranched chains. Interestingly, as the size of the clusters increases, the number of terminal side chains decreases. This finding is consistent with the belief that within the asphaltic fraction of a single crude, the average size of the aromatic clusters increases with molecular weight and a larger number of aliphatic side chains are required to link the clusters together.

X-ray diffraction data indicate that the asphaltene molecules consist of clusters of aromatic rings condensed in flat sheets connected by saturated carbon chains or a loose net of naphthenic rings. Ergun and Tiensuu (27) believe that it is not unlikely that heteroatoms replace some of the carbons in the sheets and that some of the rings may be partially saturated. Yen, Erdman, and Pollack (109) state that if the asphaltic polymer consists of islands of condensed

aromatic rings tied together with chains or saturated rings, then as the islands become smaller, the proportion of saturated structures around the aromatic islands might reasonably be expected to increase.

Empirical formulas for the asphaltenes of four asphalts have been reported by Griffin, Simpson, and Miles (35) and by Bestougeff and Bargman (9), who postulate the existence of four or five membered rings. Structures of asphaltene molecules have also been described by Hillman and Barnett (42) and by Murphy (71).

Barth (8) reports that the resins fraction is dark-colored, heavy, very adhesive, and solid or semi-solid, although it becomes very fluid on heating. The molecular weight of the resins varies from about 800 to 2000. Resins contain some sulphur, nitrogen, and oxygen. Knowles *et al.* (56), Bestougeff and Bargman (9), and Hillman and Barnett (42) have found that the carbon-hydrogen ratio varies from 0.5 to 0.85 depending on the source of the asphalt. Polycondensed rings are evident in resins with longer or more numerous alkyl side chains than the asphaltenes since less than 35 per cent of the carbon is in ring form. The resins contain proportionately more saturated than aromatic structure according to Barth (8). Hypothetical structures for resin molecules have been proposed by Gardner and his coworkers (32) that exhibit chain branching of alkyls attached to rings, which could form a large molecular interlocking network, spatially equivalent to cyclization. A proposed chain structure for resins and asphaltenes consists of polycyclic nuclei linked together by carbon atoms or possibly by oxygen or sulphur atoms (42).

The oils fraction is white in color and may, in general, be considered to consist of a mixture of saturated hydrocarbons in the molecular weight range of 360 to 800 (8). They are composed of single or condensed naphthenic rings (two to five rings per molecule) with several side chains of varying lengths, although Rossini (87) has proposed a structure that includes aromatic rings. The carbon-hydrogen ratio of asphaltic oils is reported to range from 0.5 to 0.6 (8, 56, 82).

The mass spectrometric study of Hood, Clerc, and O'Neal (47) gives evidence that the high boiling petroleum fractions are complex mixtures of rather simple high molecular weight molecules. Their work on petroleum fractions of less than 40 carbon atoms indicates that only one polyaromatic nucleus occurs per molecule. Evidence is inconclusive as to whether this also applies to naphthenic nuclei. Only one long paraffinic chain is attached to this nucleus; furthermore, there is no appreciable branching in this chain. Other aliphatic groups attached to the nucleus are short; in fact most are methyl groups. If this evidence is extended to asphalt a picture of the lighter components of the bitumen mixture is obtained.

#### C. Fractionation by Chromatography

The use of chromatography, or selective adsorption on a solid adsorbant, provides an experimentally convenient and reproducible method of fractionating asphalts into components.

Fractions obtained in this manner can be related on a chemical composition basis since Stewart (100) and Busot (14) have shown that the infra-red spectra of the same fraction obtained from different asphalts are quite similar although the relative quantities of that fraction may vary widely.

Kleinschmidt (54) developed a chromatographic method using fuller's earth as an adsorbant, obtaining four fractions called asphaltenes, water-white oils, dark oils, and asphaltic resins. An infra-red analysis of fractions obtained by Kleinschmidt's method has been reported by Stewart (100). The water-white oils fraction was seen to be predominately saturated aliphatics with some cycloparaffin and a slight aromatic content. The dark oils are highly aromatic in nature with some aliphatic structure also present. The existence of O-H, C=O, and C-O groups was also reported in the dark oils. The asphaltic resins are even more aromatic than the dark oils and appear to contain more C=O groups. The asphaltene fraction shows both aromatic and aliphatic groups. The results also indicate the existence of C=O and C-O groups but no O-H or N-H groups in the asphaltenes.

Middleton (70) used alumina chromatography to obtain six fractions: saturates, mono and dinuclear aromatic oils, polynuclear aromatic oils, soft resins, hard resins, and asphaltenes. Corbett and Swarbrick (17) used Porocel to obtain three fractions: asphaltenes, aromatics, and paraffinics + naphthenics. Other chromatographic methods of separation have been developed by Schwartz

and Brasseaus (92), Kask and Korv (52), Havens and Daniels (39), Kikuchi and Minoru (53), Schweyer, Chelton, and Brenner (93), Psalomschchikova (84), and Ziehmman (112). The asphalts used in this research were fractionated by a method developed by Schweyer and Chipley (94). The procedure of Schweyer and Chipley, which is a modification of that of Corbett and Swarbrick, utilized Porocel chromatography to obtain four fractions: asphaltenes, high aromatics, low aromatics, and paraffinics + naphthenics. The asphaltene fraction is that which is insoluble in normal hexane; the paraffinic + naphthenic fraction is that which is eluted from Porocel with normal heptane; the low aromatic fraction is eluted with benzene and the high aromatic with butanol.

#### D. Fractionation by Solvent Extraction

Fractionation by selective solvents has been a popular method of separating asphalt into components. Methods of separation employing this technique have been developed by Hoiberg and Garris (45), Listengartern and Sarukhanova (60), Hubbard and Stanfield (49), Garwin (33), and Eisenlohr and Wirth (25). The asphalts used in this research were fractionated by a method developed by Traxler and Schweyer (103) into asphaltics, saturates, and cyclics. The asphaltics is that fraction precipitated from normal butanol extraction at 122 °F. using a solvent to sample ratio of 20 to 1. The saturates are the raffinate from an acetone extraction of the normal

butanol extract using a solvent to sample ratio of 35 to 1 at  $-10^{\circ}$  F. The cyclics are the remaining fraction which is recovered from the acetone extract.

Romberg, Nesmith, and Traxler (86) have analyzed the Traxler-Schweyer fractions of three asphalts of widely varied composition for percentage carbon in aromatic,  $\text{CH}_3$  and  $\text{CH}_2$  groups. They found that the major part of the aromatic structure was contained in the asphaltic fraction and the least amount in the saturate fraction. About three times as much carbon was contained in  $\text{CH}_2$  as in  $\text{CH}_3$  for all three fractions of all three asphalts.

Gardner and his coworkers (32) have developed a method of fractionating asphalts employing thermal diffusion; Lysikhina (62) has developed a method of successive coagulation, and Csanyi and Bassi (18) an electrical potential method. O'Donnell (77) has developed a method of separation using high vacuum distillation, chromatography, thermal diffusion, selective solvents, urea complexing, and chemical reactions.

#### E. Asphalt Reactions

Asphalt undergoes a number of chemical reactions, some of which have been studied but the majority of which have not or, indeed, even been defined. The most common asphalt reaction is the air blowing reaction in which asphalt reacts with oxygen in what is thought to be primarily a combined dehydrogenation and polymerization

reaction. Asphalt also reacts with other elements of Group IV-A, sulphur, selenium, and tellurium (8). Since the reactions with air and sulphur are those that were studied in this research they will be discussed at length later.

Asphalt has been reacted with hydrogen chloride, boron trifluoride, and silicon hexafluoride by Nellensteyn and Mareeuw (75), carbon dioxide by Garbalinski and Sergienko (31), and hydrogen by Szucs and Ackermann (101). Halogens have been reacted with asphalt by Mariano (68), Nellensteyn and Dorleyn (74), and Marcusson (67) and found to give both addition and substitution products. Several processes for reacting halogens with asphalt have been patented (28, 21, 72).

Asphalt can be reacted with sulphuric acid to form sulphonates and sulphuric acid esters according to Marcusson (67) and Gurwitch (38). Nitration forms products of the nature of phenyl nitromethane and nitrohydrocarbons and oxidation with permanganate forms acids. The asphaltene fraction is known to form molecular complexes with such inorganic compounds as ferric chloride and mercuric bromide (8) and the cyclics present in asphalt are known to undergo aldehyde condensation (73). Other reactants that have been used with asphalt are alkalis, phosphorous, nitric acid, phosphoric acid, formaldehyde, furfural, and metallic salts (29).

#### F. The Air Blowing Reaction

The air blowing reaction consists of many different types of reactions taking place simultaneously at the interface of the

liquid asphalt and the air bubble rising through the asphalt. Since this reaction is of such industrial importance, there are many references in the literature concerning air blowing, but few of them are concerned with the chemical nature of the reactions taking place.

Kinetic studies of air blowing have been undertaken by Holmgren (46) and Ariet (6). A low energy of activation value indicates that the reaction is diffusion controlled, especially at lower temperatures. This is further substantiated by Rescorla's (85) finding that agitation during air blowing reduces the blowing time considerably. Lockwood (61) reports that the reaction can be considered first order except at high temperatures and low flow rates. Ariet (6) found that at a temperature of around 550 °F. the rate also becomes a function of the concentration of the asphaltic fraction.

The air blowing reaction is thought primarily to consist of dehydrogenation and polymerization reactions along with the formation of oxygenated hydrocarbons. A comprehensive study of air blowing has been presented by Goppel and Knotnerus (34). They report that the major part of the oxygen reacting with asphalt is found in the exit gas, mainly as  $H_2O$  but to a small extent also as  $CO_2$ , which agrees with Labout's (57) report that as much as 80 to 90 per cent of the reacting oxygen is converted to water at high temperatures. The remaining reacted oxygen is bound in functional groups in the

asphalt, primarily hydroxyl, acid, carbonyl, and ester groups. No ether formation was reported, a finding that contradicts Marcusson (64, 65, 66) and Sachanen (91) but is substantiated by the work of Liiv (59). The proportion of the reacting oxygen which becomes bound in functional groups is reported to be a function both of the composition of the asphalt and the processing conditions. Asphalts of low aromaticity can be dehydrogenated to a larger extent than the more aromatic types, but a larger percentage of oxygen forms functional groups in the aromatic type asphalts.

The formation of ester bonds is of particular importance, not only because they account for nearly 60 per cent of the oxygen in functional groups, but also because ester linkage may be one of the more important polymerization reactions occurring in the air blowing process. At a temperature of 250 °C. Goppel and Knotnerus (34) report that as many ester bonds as direct carbon-carbon bonds are formed, although at 350 °C. five times as many carbon-carbon bonds are formed. The reduced number of ester groups as well as acid groups at higher temperatures is attributed to the decomposition of the carboxylic groups. This is verified experimentally by the increasing concentration of water and carbon dioxide in the exit gas at high temperatures.

Other reactions that have been proposed by Marcusson (64) to take place during the air blowing reaction are the formation of asphaltogenous acids and anhydrides of a somewhat cyclic character,

the oxidation of hydrocarbons to hydroxyl derivatives, followed by separation of water to form an ether, and the inter molecular loss of carbon dioxide from an anhydride to yield a ketone.

Analyses of the changes in the various fractions of asphalt during air blowing have been reported by Eng, Glovier, and Quon (26), Kleinschmidt and Snoke (55), and Gun (36). All reports indicate an increase in the concentration of asphaltenes, an increase in molecular weight, and an increase in unsaturation, but aside from these there is no consensus on the effect of air blowing on asphalt composition.

Sergienko and his coworkers (95) have found that paraffins, cycloparaffins, and monocyclic aromatic hydrocarbons are converted to condensed bicyclic hydrocarbons, polycondensed aromatic hydrocarbons, and asphaltenes. Polymerization by cross linking is reported by Murphy (71) along with the formation of volatile products by oxidative cracking. Gun (37) has shown that the naphthenic rings are susceptible to dehydrogenation, but not the side chains. However, the side chains are susceptible to oxidation according to Eng, Glovier, and Quon (26) and Zabauin (111).

#### G. Catalytic Air Blowing

The literature on catalytic air blowing consists almost entirely of either proposals of various new catalysts for air blowing and their effect on the blowing time or the physical properties of the product, particularly the softening point-penetration curve, or

reviews of the subject of catalytic air blowing with the emphasis on the various types of catalysts that have been used and industrial processing conditions. There is some doubt as to whether the various additives are actually catalysts since some of them are believed to combine chemically with the asphalt during air blowing. Alexander and Shurden (3) report that the chemical state of ferric chloride is unchanged in the air blowing process and can be recovered by extraction with water, while phosphorus pentoxide seems to become an integral part of the asphalt molecule and is not water extractable. Shearon and Hoiberg (97) have found that as air blowing proceeds, discrete particles of  $P_2O_5$  disappear, presumably to form a water resistant complex.

Hoiberg (44) has written a rather comprehensive review of catalytic air blowing, in which he lists the effects of 31 different catalysts on blowing time and penetration of the asphalt. However, the questions regarding the types of reactions that these catalysts preferentially retard or accelerate to obtain the desired change in properties remain totally unanswered.

#### H. The Sulphur Reaction

The reaction of sulphur with asphalt likewise has been given little attention. It is generally thought to be primarily a dehydrogenation reaction with some polymerization and addition to the double bonds formed by dehydrogenation.

Although it is generally accepted that sulphur dehydrogenates the asphalt to form olefinic double bonds, it is also known that olefins are quite reactive with sulphur. Brooks (10) reports that olefins are not found among the reaction products of paraffins with sulphur in liquid phase reactions, probably because the olefins react faster with sulphur than saturated hydrocarbons. Westlake (107) cites evidence of Friedmann (30) and Armstrong, Little, and Doak (7) to show that the sulphur adds alpha to the double bond of a long chain hydrocarbon forming a mercaptan intermediate which reacts with another olefin to form an unsaturated sulphide. This process could then be repeated, resulting in polymerization by sulphur linkage.

Horton (48) has studied the reactions of alkylaromatics with sulphur and has found that when alkylaromatics are heated at 200 to 250 °C. with sulphur, dimerization reactions occur. The first reaction he reports involves the carbon-carbon linkage of two aliphatic side chains with the evolution of hydrogen sulphide. The second dimerization reaction is similar except that linkage is by an olefinic double bond. The third polymerization reaction described can be accomplished by four methyl aromatics linking to form a thiophene type structure with aromatics at each of the four carbons of the thiophene ring. Since asphalt contains many alkylaromatic type compounds, it is possible that these types of reactions are at least partially responsible for the polymerization that is considered to take place.

Pryor (83) reports that sulphur abstracts hydrogen from organic compounds at 200 to 300 °C. to give stable products by aromatization and ring formation with most of the sulphur forming hydrogen sulphide but some being incorporated into the product. Ruzicka and Meyer (89) and Ruzicka, Meyer, and Mintazzini (90) have found that naphthenic rings are dehydrogenated all the way to aromatic rings at temperatures above 200 °C. Side chains of sufficient length (four or more carbon atoms) can be closed to form aromatic structures or thiophene type structures. The latter is more common in aliphatic side chains. The rate of reaction of sulphur with paraffinic chains generally increases with the length of the chain and the amount of branchiness according to Brooks (10). Higher temperatures (above 600 °C.) are required for complete oxidation to carbon disulphide.

### I. The Heat of Reaction

The heat of reaction of air blowing has long been of interest to asphalt technologists because of the fact that in industrial air blowing, the removal of the exothermic heat of reaction is an important processing problem. While a great deal of speculation has been made as to the magnitude of the heat of reaction, the only work published on this subject is one by Smith and Schweyer (98) on an empirical basis using the change in the ring and ball softening point as a parameter. Such a determination is valuable for design

calculations but of little value in theoretical considerations. Research on the heat of reaction of other asphalt processes has not been attempted on any basis.

If a measurement of the heat of reaction of processing asphalt could be obtained, then its magnitude would lend some insight into the nature of the reactions occurring. If the value calculated for the heat of reaction of a proposed reaction from the heats of formation of products and reactants is of the order of magnitude of the experimentally measured value, this would be further evidence that this type of reaction might indeed be occurring. However if the calculated value of the heat of reaction deviates greatly from the experimentally measured value, then perhaps these reactions are not as important as they had been proposed.

Furthermore, if the experimentally measured value of the heat of reaction was different for asphalts of difference composition, then it would follow that different types of reactions take place when processing different asphalts or that certain reactions play a more important role with different asphalts. The effect of processing conditions such as temperature or extent of completion of the reaction on the magnitude of the heat of reaction could be determined and related to a variation in the types of reactions occurring since different reactions would have different heats of reaction. In this way additional information concerning the reactions occurring at different temperatures and at different stages in the reaction could be obtained.

The effect of catalysts on the magnitude of the heat of reaction is quite important since not one but many reactions are occurring during processing. If the addition of a catalyst changes the magnitude of the heat of reaction, this could lend a definite insight into its preferential acceleration or retardation of certain types of reactions.

## CHAPTER III

### EXPERIMENTAL

#### A. Design of the Process

The experimental work was carried out in equipment specifically designed and built for the purpose of measuring the heat of reaction of asphalt air blowing, catalytic air blowing, and sulfurization. The reactor itself was designed to react about five gallons of asphalt in a batch process. Additional process equipment includes a drying column to remove the moisture from the incoming air and an air preheater to heat the inlet air to reaction temperature.

The removal of the aerosol that is formed in the exit gases of the air blowing reaction was necessary before the exit stream could be run through a flowmeter and a gas analyzer. Two additional pieces of equipment were required to solve this difficult processing problem. The first was an electrostatic precipitator, which, with an applied potential of 30,000 volts on the electrode, would remove about 99 per cent of the aerosol, which would then collect in the bottom of the precipitator as an oily product. A study of the chemical nature of these oils has been made by Busot (13), who

postulated that the aerosol was formed by the condensation of the more volatile components of the asphalt, which vaporize during the air blowing. The small amount of aerosol that was not removed by the precipitator, which would still foul the analysis equipment, was found to adhere to glass or ceramic surfaces on contact. Consequently a column filled with ceramic Berl saddles subsequent to the precipitator would remove all detectable traces of the aerosol. Two heat exchangers to cool the exit gas stream, one preceding the precipitator and one between it and the Berl saddle column, were included in the design. An exit gas analysis by-pass line that sends the exit gas and aerosol directly to the stack was added to permit continuous operation of the reactor through short time failures in the precipitator. A picture of the equipment is presented as Figure 1 and a flow diagram of the process is included as Figure 2.

#### B. Design of Equipment

The reaction vessel is of stainless steel construction, a section of schedule 40 pipe, 14 inches in diameter and 20 inches in height. When charged it is about half full of asphalt, the remaining volume being available for separation of entrained asphalt from the exit gas. A 3000-watt Chromalox immersion heater type MTS-230B is installed in the side of the reactor for the purpose of heating the asphalt charge to reaction temperature. A thermowell in the reactor side permits the measurement of the

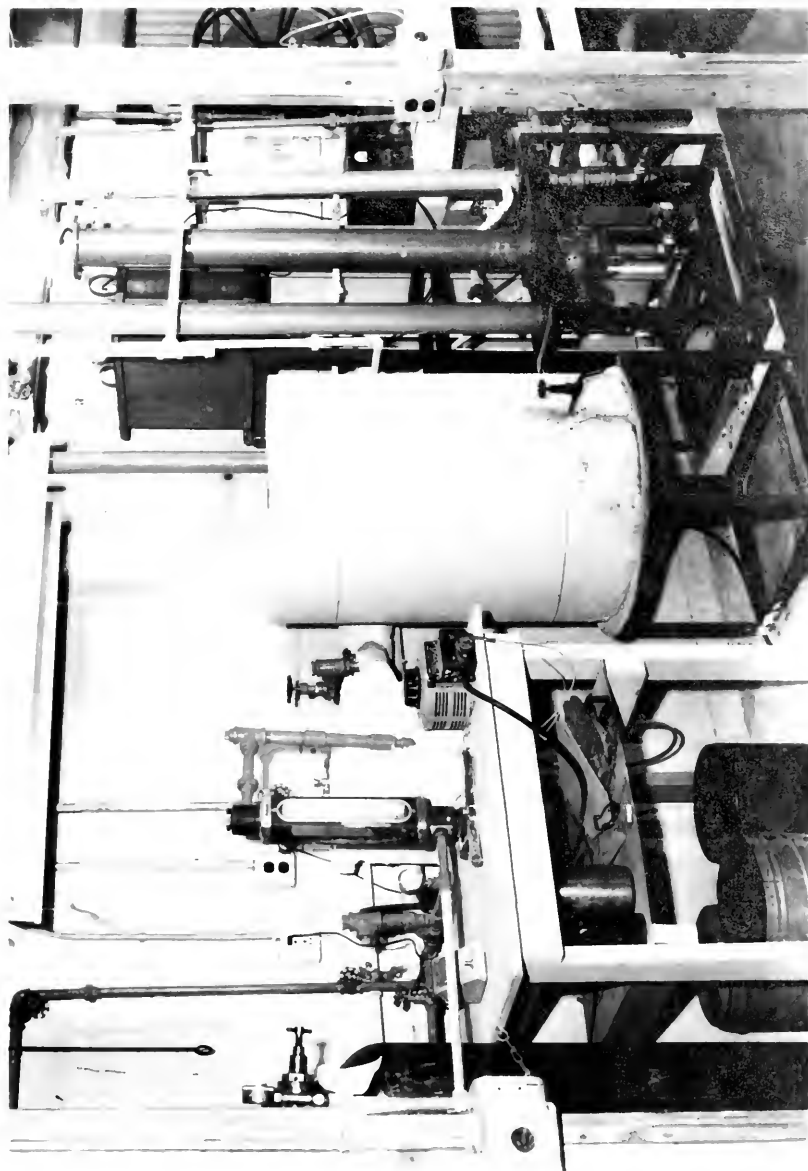


Figure 1. Experimental Processing Equipment



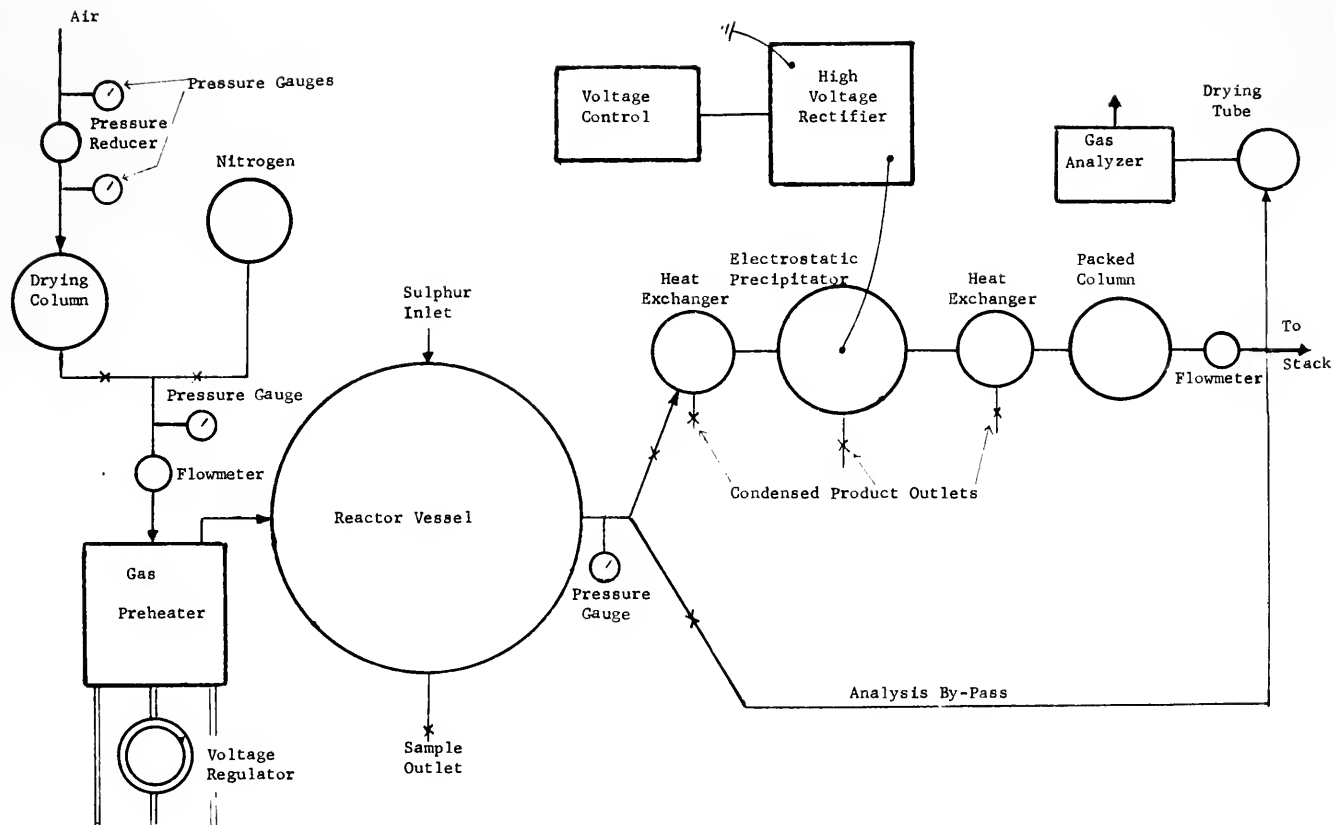


Figure 2. Schematic Diagram of Apparatus

reaction temperature. A gas disperser, which is 1/2-inch stainless steel tubing with 1/32-inch downward facing holes spaced 1 inch apart, is coiled in the bottom of the reactor to ensure that complete mixing takes place. A 3/8-inch sampling outlet is installed near the bottom of the reactor and a 3/4-inch outlet in the bottom permits draining at the completion of the run.

The reactor cover is a flat 1/4-inch stainless steel plate, which is bolted to the reactor. The outlet line for the exit gases is a 2-inch pipe in the top of the reactor. Its large size minimizes any entrainment of liquid asphalt in the exit gases. In this exit line is placed a sulphur injection port that provides the means of adding liquid sulphur to the hot asphalt. A Black, Sivalis, and Bryson safety head with a 2-inch aluminum disk in this line reduces the possibility of an explosion due to an increase in pressure. The reactor is completely insulated with six inches of Johns-Manville Thermobestos insulation. A drawing of the reactor is included in Appendix A.

The air preheater was designed to elevate the temperature of the incoming air to the temperature of the reactor. The preheater consists of a steel box containing six compartments. The opening to each compartment is so placed that the incoming air must go through a tortuous path from compartment to compartment before leaving the preheater to achieve maximum heat transfer. In each compartment



is a 1000-watt conical heating element. These heating elements are wired in series to three 220-volt circuits, two heaters in each circuit. To keep the box airtight the current carrying high temperature fiberglass insulated nichrome wires enter the box through ceramic sealed Conax thermocouple glands. The only control on two circuits is off-on, but the other circuit contains a voltage regulator so that the voltage of this circuit can be controlled over the entire range of 0 to 220 volts. Temperature control of the air entering the reactor is maintained by this voltage control of the preheater heating elements. The preheater and gas line leading to the reactor are also well insulated. A drawing of the preheater is shown in Appendix A.

The drying column was designed to contain a quantity of silica gel sufficient to dry the quantity of air that would be used in the longest run, thereby eliminating the necessity of reactivating the silica gel in the middle of a run. It consists of a 4-inch Lucite column 51 inches long on an angle iron stand with a coupling at the top to the 1/2-inch line containing air from the compressor reduced to a gauge pressure of 25 pounds per square inch.

Before entering the preheater the inlet gas first passes through a Fisher-Porter Precision Bore Flowmeter. The inlet gas can be either the dry air from the silica gel column or nitrogen. The air is used as the reactant and the nitrogen is used as an inert to mix the asphalt prior to initiating the reaction with air or sulphur, to mix the asphalt at the completion of the sulphur run, and to obtain cooling curves, by which the heat loss of the system can be evaluated.

By means of valves it is possible to switch immediately from air operation to nitrogen operation.

The electrostatic precipitator consists of a 4-inch steel pipe 60 inches in length. A bakelite cover is bolted to a flange at the top of the column. Through this cover and a high voltage ceramic bushing is extended the high voltage electrode, a 1/4-inch steel rod. The aerosol enters the precipitator at the bottom through a baffle arrangement that ensures that the aerosol is well distributed in the precipitator. The lower extremity of the electrode is secured to a glass insulator attached to the center of the baffle. The precipitated aerosol collects as an oil in the bottom of the precipitator below the inlet baffle and can be removed by opening a valve at the bottom.

The voltage source is a Carpco Model RI high voltage rectifier, which supplies a voltage that can be varied from 0 to 40,000 volts with a current output of 12 milliamperes on dead short circuit to ground.

The packed column containing the Berl saddles to remove the last of the aerosol was constructed from two sections of pipe joined by a bell reducer. The lower section is a 3-inch steel pipe and the upper section is a 2-inch steel pipe. The total length of the column is 73 inches. A drain in the bottom of the column was included to permit drainage of the collected oils but this proved useless since the oil adhered to the surface of the Berl saddles and would not flow to the bottom. Consequently it was necessary to empty the column and clean the packing about every three or four runs.

The heat exchangers are the concentric tube type with cooling water in counter current flow on the shell side. The first, which precedes the precipitator, consists of a 1 1/2-inch steel pipe inside a 3-inch steel pipe 60 inches in length and the second, which follows the precipitator, is a 3/4-inch steel pipe inside a 2-inch steel pipe 48 inches in length. Since water condensed in the first exchanger and a limited amount of aerosol precipitated in both exchangers, valves were installed in the bottom ends of the heat exchangers. The entire apparatus is mounted on 1 1/2 x 1 1/2 x 1/4-inch angle iron framework. Drawings of the heat exchangers, as well as the electrostatic precipitator drying column, and surface column, are included in Appendix A.

#### C. Experimental Design for Air Blowing

The air blowing experiments were statistically designed to measure the effects of three factors on the heat of reaction. The first factor was the type of asphalt. For this, three different asphalts were selected: an East Texas asphaltic residuum, a Gulf Coast naphthenic residuum, and a West Texas-New Mexico residuum. They were chosen because they represent different composition types and the effect of the type of asphalt on the heat of reaction, if significant, could be expected to appear in the results of reacting these asphalts. A list of the properties of these three asphalts is presented in Table 1.

TABLE 1

## ASPHALT PROPERTIES

	East Texas Asphaltic Residuum	Gulf Coast Naphthenic Residuum	West Texas New Mexico Residuum
Identification	S-62-2	S-62-3	S-63-3
Specific Gravity, 60/60 °F.	1.015	0.957	1.010
Kinematic Viscosity, Stokes, 210 °F.	12.3	2.58	12.7
140 °F.	300	30	405
Penetration, 77 °F. 100/5	275	too soft	184
Ring and Ball Softening Point, °F.	98	70	100
Sulphur Content, %	3.94	0.66	2.64
Oxygen Content, %	0.38	0.23	0.71
Component Analysis (a)			
Asphaltics, %	42.0	15.6	36.0
Saturates, %	44.0	68.2	51.0
Cyclics, %	14.0	17.2	13.0
Component Analysis (b)			
Asphaltenes, %	10.5	0.5	2.2
High Aromatics, %	31.7	22.0	37.7
Low Aromatics, %	45.5	41.5	48.4
Paraf. + Naphth., %	12.3	36.0	11.7

(a) Determined by method of Traxler and Schweyer (103).

(b) Determined by method of Schweyer and Chipley (94).

The second factor to be studied was the extent of the completion of the air blowing process; that is, to determine if the heat of reaction changed significantly as the air blowing proceeded. As an indication of the extent of completion, the ring and ball softening point was selected. The ring and ball softening point is measured by a method described by the American Society for Testing Materials Test D 36-26. The softening point is a measure of the consistency of the asphalt and is known to increase approximately linearly with time as air blowing proceeds. From Table 1 it can be seen that the softening point of S-62-3 is 70 °F., considerably below those of S-62-2 and S-63-3, which are 98 and 100 °F., respectively. The levels of softening point that were considered were 100 to 130 °F., 130 to 180 °F., and 180 to 250 °F. for all three asphalts. In addition the range 70 to 100 °F. was considered for asphalt S-62-3.

The third factor to be studied was reaction temperature. Since the experimental method requires approximate adiabatic operation with the only loss of heat due to normal convection heat losses from the outside of the insulation, isothermal operation was not feasible. Therefore two ranges of temperature were selected as the temperature factors. The first range was from 460 to 475 °F., which is the lower end of the temperature range at which asphalt is usually processed and the second was from 535 to 550 °F., which was the upper end of the range.

For this type of operation a factorial experimental design will reveal the most statistical evidence with a minimum of experimental data. A requirement of the factorial design is that all levels

of each factor must be the same for all other factors; that is, the temperature and softening point ranges must be identical for all three asphalts. This condition is satisfied if the softening point range, 70 to 100 °F. for asphalt S-62-3, is not considered in the analysis of variance. In this factorial design there are three levels of asphalt, three levels of softening point, and two levels of temperature, hence it is designated a  $3 \times 3 \times 2$  factorial design.

The analysis of variance for the factorial reveals the significance of both simple effects and interactions. A simple effect is the difference in response over different levels of the same factor, while an interaction of two or more factors is the difference in the simple effects of those factors. If these effects differ by more than can be attributed to chance at the 95 per cent confidence limit, the difference is said to be significant. If the difference is greater than can be attributed to chance at the 99 per cent confidence limit, the difference is said to be highly significant.

#### D. Operating Procedure for Air Blowing

A weighed quantity of asphalt (43 to 50 pounds) was charged to the reactor and the charge was heated until it had reached a temperature about 30 degrees higher than the desired temperature range. Nitrogen was bubbled through the reactor at a low flow rate to mix the asphalt, thereby ensuring that the asphalt temperature was uniform throughout the reactor. The heater was disconnected and

temperature readings of both the incoming nitrogen and the asphalt charge were made every five minutes with the nitrogen temperature being regulated to the same temperature as the asphalt. When the temperature of the asphalt had dropped to the lower limit of the temperature range (460 or 535 °F.), the incoming nitrogen was replaced by air, which reacted with the asphalt. The exit gas went through the heat exchangers, electrostatic precipitator, and the packed column to a Fisher-Porter flowmeter, where the flow rate of the aerosol free gas was measured. The gas stream was then split with the majority going to the stack and the remainder being passed through a small silica gel column, where the moisture as well as remaining traces of aerosol were removed. The gas then entered a Beckman Model C oxygen analyzer to determine its oxygen content.

As the reaction proceeded the asphalt temperature rose because of the liberation of the exothermic heat of reaction. During this period readings were made every five minutes of asphalt temperature, inlet flowmeter position, incoming air temperature and pressure, the pressure on the system, outlet flowmeter position, exit gas oxygen content, and ambient air temperature. As soon as the temperature of the asphalt approached the upper limit of the temperature range (475 or 550 °F.), the air was replaced by nitrogen, causing the temperature of the asphalt to drop again due to normal heat losses of the system. When the asphalt temperature again approached the lower

limit of the temperature range, air was reintroduced, the reaction was reinitiated, and the temperature of the charge again rose. This procedure was repeated until the reaction had slowed to the point at which the exothermic heat of reaction was no longer sufficient to maintain the asphalt at reaction temperature. A time-temperature profile from a typical run is illustrated in Figure 3. Each point on the graph is an experimental value of the asphalt temperature.

During the latter part of the reaction at the lower temperature range, the rate of reaction was not sufficiently rapid to keep the temperature above the lower limit of the temperature range. In this case it was necessary to reheat the asphalt to the upper limit and obtain data as the system cooled while reacting until the softening point of 250 °F. was reached.

Samples were taken approximately every hour during the reaction and were measured for ring and ball softening point. Selected samples were analyzed for oxygen content to determine the percentage of reacting oxygen actually chemically bound in the asphalt. These values are reported in Appendix I.

The amount of heat liberated during each incremental rise could be calculated as well as the total amount of oxygen consumed. In this way the heat of reaction per mole of oxygen was calculated for each increment. A total of twelve runs was required for this part of the research, two duplicate runs of each of the three asphalts over the two temperature ranges. A table of all the experimental data is given in Appendix I.

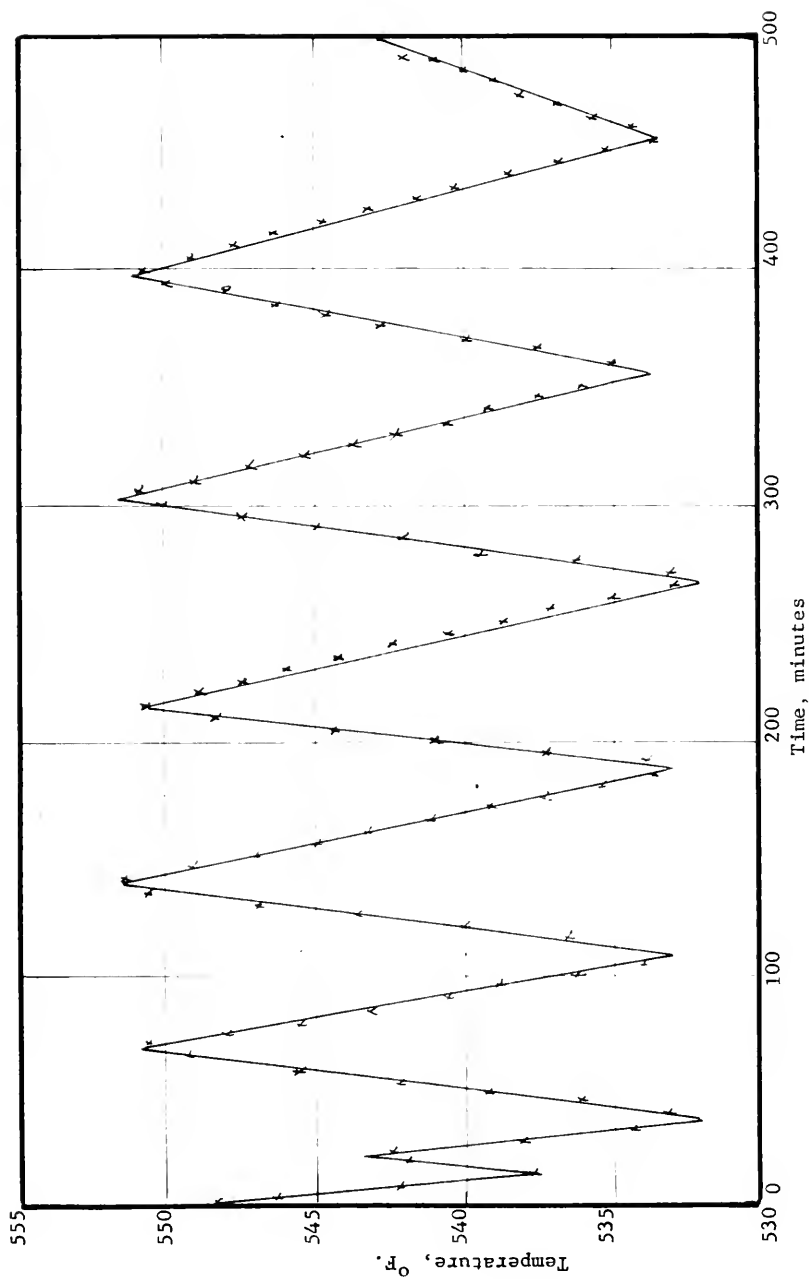


Figure 3. Time-Temperature Profile,  $T = f(t)$ , Run R-63-6

### E. Experimental Design for Catalytic Air Blowing

To determine the effect of catalysts on the heat of reaction of air blowing asphalt, two of the most common catalysts, aluminum chloride and phosphorus pentoxide, were selected. A third catalyst, ferric chloride, was also selected but experimental difficulties forced the discontinuance of work with this catalyst.

Since the type of asphalt, temperature, and extent of completion of the reaction were not factors in this part of the research, a different statistical design was required. The most meaningful results with the minimum of experimental data could be obtained by applying a method developed by Dunnett (23). The objective of Dunnett's procedure is to compare several treatments with a standard. For this study the standard was taken to be the heat of reaction of air blowing asphalt S-62-3 over the softening point range of 70 to 130 °F. Since two duplicate runs of air blowing S-62-3 at the temperature ranges of 460 to 475 °F. and 535 to 550 °F. were completed in the first part of this research, and, as can be seen in Table 8, there was little effect of temperature on asphalt S-62-3, four replicate values of a standard had already been obtained. By air blowing asphalt S-62-3 over the temperature range 460 to 550 °F. with aluminum chloride and phosphorus pentoxide with duplicate runs for each catalyst, the five degrees of freedom required for Dunnett's test are obtained.

The experimental procedure for catalytic air blowing is identical to that for ordinary air blowing except that 2 per cent catalyst was added to the asphalt and that the reaction was initiated at a temperature of 460 °F. and allowed to elevate the temperature to 550 °F., at which point a softening point of approximately 130 °F. had been obtained and the reaction was terminated.

The elimination of temperature as a factor and consequently the need for alternate nitrogen and air operation, as well as the termination of the run at a softening point of 130 °F. instead of 250 °F., considerably decreased the time required to complete an experimental run.

#### F. Experimental Design for Sulphurization

Because the reaction of asphalt with sulphur is endothermic rather than exothermic, as is the case in air blowing, and because sulphur reacts as a liquid rather than a gas, a different experimental procedure was required. The only factor to be considered in the sulphur reaction was the type of asphalt. With the heat of reaction of the three asphalts, the East Texas, the Gulf Coast naphthenic, and the West Texas-New Mexico, to be measured and studied, an experimental design utilizing the F-test was appropriate.

In the procedure adopted, the reactor was charged and heated to about 575 °F. as in air blowing. Ten parts per million of Dow Corning Fluid dissolved in 30 milliliters of kerosene was added to eliminate the foaming that was found to occur when the asphalt and

sulphur reacted. Nitrogen was bubbled through the asphalt at a low flow rate to ensure uniform temperature. The heat was cut off, and when the temperature of the asphalt dropped to about 550 °F., the nitrogen was shut off and a weighed quantity of liquid sulphur (about 1200 grams) was added in approximately 200 gram increments. The ensuing reaction was very rapid with hydrogen sulphide given off at a high rate. After the aerosol mist in the exit gas, which appears to a lesser extent than in air blowing, had been removed, the flow rate was measured by the exit gas flowmeter. In a few minutes the reaction would subside and an additional increment of sulphur was added. This was repeated until all of the weighed quantity of sulphur had been added.

When no further evolution of hydrogen sulphide could be detected (about 15 minutes after the addition of the last increment of sulphur), nitrogen was readmitted to the asphalt to keep the system well mixed and at uniform temperature throughout. Temperature readings of the system were recorded every five minutes and the temperature at this point was usually between 470 and 480 °F. After 10 to 15 minutes of operation with nitrogen bubbling through the asphalt, it was assumed that all of the sulphur had been reacted. The heat consumed during this entire operation could be calculated, hence the heat of reaction per mole of sulphur consumed could be determined. The asphalt was reheated to 550 °F. and the procedure repeated with another weighed quantity of sulphur. In this manner fifteen values of the heat of reaction were obtained from six runs.

## CHAPTER IV

### CALCULATION PROCEDURE

#### A. The Heat Balance

The quantity of heat liberated over an incremental reaction range was determined by making a heat balance on the system

Input - Output + Generation = Accumulation

$$H_a - H_o - L + Q = A_{as} + A_r + A_i \quad (1)$$

$$Q = A_{as} + A_r + A_i - (H_a - H_s) + L \quad (2)$$

where

$H_a$  = Enthalpy of entering air, BTU

$H_o$  = Enthalpy of exit gases, BTU

$L$  = Heat Losses, BTU

$Q$  = Heat generated by the reaction, BTU

$A_{as}$  = Accumulation of energy in the asphalt, BTU

$A_r$  = Accumulation of energy in the reacting vessel,  
BTU

$A_i$  = Accumulation of energy in the insulation, BTU

### B. Evaluation of Input and Output Terms

The input and output terms of the heat balance were evaluated in the following manner.

$$H_a = F_a C_a (T_a - T_d) \Delta t \quad (3)$$

where

- $F_a$  = Mass flow rate of air, lb. min.<sup>-1</sup>  
 $C_a$  = Heat capacity of air, BTU lb.<sup>-1</sup> °F.<sup>-1</sup>  
 $T_a$  = Temperature of incoming air, °F.  
 $T_d$  = Arbitrary datum temperature, °F.  
 $t$  = Time, min.

$$H_o = F_o C_o (T_o - T_d) \Delta t \quad (4)$$

where

- $F_o$  = Mass flow rate of exit gas, lb. min.<sup>-1</sup>  
 $C_o$  = Heat capacity of exit gas, BTU lb.<sup>-1</sup> °F.<sup>-1</sup>  
 $T_o$  = Temperature of exit gas, °F.

Since the exact composition of the exit gas was unknown, the value of the heat capacity of the exit gas stream could not be determined. The assumption was made that

$$F_o C_o = F_a C_a \quad (5)$$

Since the incoming air is 80 per cent nitrogen, which is inert, and no more than 30 per cent of the oxygen reacts, this assumption could not be in error by more than 7 per cent. It was also assumed that thermal equilibrium was approached between the air and asphalt during the reacting period so that the temperature of the

exit gas was the same as the temperature of the asphalt (that is,  $T_o = T_{as}$ ). In a thoroughly mixed system this assumption is a valid one. Then

$$H_a - H_o = F_a C_a (T_a - T_{as}) \Delta t \quad (6)$$

where

$$T_{as} = \text{Temperature of the asphalt, } ^\circ\text{F.}$$

By maintaining the inlet air temperature close to the temperature of the asphalt, this term can be made small, justifying the assumptions made.

### C. Evaluation of Accumulation Terms

The accumulation terms are evaluated by the following procedure

$$A_a = M_{as} C_{as} (T_2 - T_1) \quad (7)$$

where

$$M_{as} = \text{Mass of the asphalt charge, lb.}$$

$$C_{as} = \text{Heat capacity of asphalt, BTU lb.}^{-1} \text{ } ^\circ\text{F.}^{-1}$$

$$T_1 = \text{Temperature of the asphalt at time } t, \text{ } ^\circ\text{F.}$$

$$T_2 = \text{Temperature of the asphalt at time } t + \Delta t, \text{ } ^\circ\text{F.}$$

$$A_r = M_r C_r (T_2 - T_1) \quad (8)$$

where

$$M_r = \text{Mass of the reactor vessel, lb.}$$

$$C_r = \text{Heat capacity of the reactor vessel, BTU lb.}^{-1} \text{ } ^\circ\text{F.}^{-1}$$

In writing equation (8) it was assumed that the thermal conductivity of the stainless steel reactor and the asphalt film coefficient were infinite, causing the temperature of the entire vessel to be the same as that of the reacting asphalt. This assumption might seem to be a rather poor one because the film transfer coefficient is known to be low. However, if it were as low as 10 BTU per (hour-degree F.-square foot), the magnitude of its resistance would be small for an over-all heat transfer coefficient of about 0.2, which was calculated for the insulated reactor, so the assumption would be justified.

The first term in equation (9) is the accumulation of energy in the insulation on the sides of the reactor and the second term is the accumulation in the top and bottom insulation.

$$A_i = 2\pi C_i \rho h \int_{R_\alpha}^{R_\beta} [T_2(r) - T_1(r)] r dr + 2\pi R_\alpha^2 C_i \rho \int_0^x [T_2(x) - T_1(x)] dx \quad (9)$$

where

- $C_i$  = Heat capacity of the insulation, BTU lb.<sup>-1</sup> °F.<sup>-1</sup>
- $h$  = Height of the reactor, in.
- $r$  = Radius, in.
- $x$  = Vertical distance from top or bottom of reactor, in.
- $R_\alpha$  = Radius of reactor, in.

- $R_{\beta}$  = Outer radius of insulation, in.  
 $\rho$  = Density of the insulation, lb. in.<sup>-3</sup>  
 $T_1(r)$  = Temperature of the insulation as a function of radius at time  $t$ , °F.  
 $T_2(r)$  = Temperature of the insulation as a function of radius at time  $t + \Delta t$ , °F.  
 $T_1(x)$  = Temperature of the insulation on the top and bottom ends of the reactor as a function of position at time  $t$ , °F.  
 $T_2(x)$  = Temperature of the end insulation as a function of position at time  $t + \Delta t$ , °F.

#### D. Solution of Unsteady State Heat Transfer Problem

Considering the first integral in equation (9), it was necessary to evaluate  $T_1(r)$  and  $T_2(r)$  as functions of radius before the integration could be carried out. These variables can be related by setting up an unsteady state heat balance, which yields a second order partial differential equation, which is given in cylindrical coordinates by

$$\frac{c_i \rho}{k} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \quad (10)$$

where

- $k$  = Thermal conductivity,  $\text{BTU min.}^{-1} \text{ } ^\circ\text{F.}^{-1} \text{ in.}^{-1}$   
 $r$  = The distance from the axis of the cylinder  
 to any point on the radius, in.  
 $\theta$  = The angle between  $r$  and the x-axis, radians  
 $z$  = The distance measured along the axis of the  
 cylinder, in.

If the assumption is made that heat transfer takes place only in the radial direction, that is,  $\frac{\partial T}{\partial \theta} = 0$  and  $\frac{\partial T}{\partial z} = 0$ , then equation (10) simplifies to

$$r \frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{\partial r} \frac{c_i \rho}{k} r \frac{\partial T}{\partial t} \quad (11)$$

The boundary conditions for equation (11) were taken as follows.

Boundary Condition 1: At  $r = R_\alpha$ ,  $T = f(t)$ , where  $f(t)$  is obtained experimentally by the temperature readings of the asphalt at five minute time intervals. A plot of  $T = f(t)$  for Run R-63-6 is shown in Figure 3.

Boundary Condition 2: At  $r = R_\beta$ ,  $T = g(t)$ , where  $g(t)$  is obtained experimentally by a knowledge of the over-all heat transfer coefficient between the outside of the insulation and the ambient air. The temperature at  $R_\beta$  can be stated as an explicit function of reactor temperature and ambient air temperature, both of which are functions of time. This calculation is shown as Appendix B.

For the initial condition, steady state is assumed at time = 0. The solution to equation (11) with  $\frac{\partial T}{\partial t} = 0$  is simply the solution of the ordinary differential equation

$$r \frac{d^2 T}{dr^2} + \frac{dT}{dr} = 0 \quad (12)$$

with the boundary conditions at  $r = R_\alpha$ ,  $T = T_{R_\alpha}$  and at  $r = R_\beta$ ,  $T = T_{R_\beta}$ .

Initial Condition: At  $t = 0$

$$T = T_{R_\alpha} - \frac{[T_{R_\alpha} - T_{R_\beta}] \ln [r/R_\alpha]}{\ln [R_\beta/R_\alpha]} \quad (13)$$

A finite difference approximation was used to solve equation (11) with the preceding boundary and initial conditions. The finite difference equation is given by

$$T_{m,n+1} = \frac{(1 + 1/m)T_{m+1,n} + (N - 1/m - 2)T_{m,n} + T_{m-1,n}}{N} \quad (14)$$

where

$$N = \frac{C_i (\Delta r)^2}{k (\Delta t)}$$

$$m = r / \Delta r$$

Increments of 1 inch for  $\Delta r$  and 5 minutes for  $\Delta t$  satisfy the stability criterion for finite difference equations (69) and were selected for use in making the calculations. The calculations for stability are presented in Appendix C.

An IBM 709 computer was employed to solve the boundary and initial conditions and to make the calculations in the finite difference solution. The computer program, written in the FORTRAN language, is included as Appendix D. After  $T_1(r)$  and  $T_2(r)$  had been obtained as functions of radius, the integration was carried out numerically.

A similar procedure could have been followed for the insulation on the top and bottom ends of the reactor but this would have involved a considerable amount of additional calculations. As an approximation, the accumulation of energy in the end insulation was assumed to be proportional to the accumulation in the side insulation with the ratio of heat transfer areas taken as the constant of proportionality.

#### E. Evaluation of Heat Losses

The rate of heat loss from the system was evaluated from the data taken while nitrogen rather than air was blown through the reactor. In this case no reaction takes place and so no heat of reaction is generated. Nine values of the heat loss were calculated for operation over the temperature range 460 to 475 °F. and 16 values for operation over the temperature range 535 to 550 °F. The average of these values was found to be 10.61 BTU per hour and 11.64 BTU per hour for the temperature ranges 460 to 475 °F. and 535 to 550 °F., respectively. The heat loss term is then simply calculated from equation (15).

$$L = L' \Delta t \quad (15)$$

where

$L'$  = Calibrated rate of heat loss, BTU min.<sup>-1</sup>

The value of  $Q$  is then obtained simply by summing all terms on the right-hand side of equation (2). A check as to the correctness of this procedure was devised by connecting a voltmeter and an ammeter across the line to the reactor heater and measuring the energy input of the heater over an incremental period similar to one that would be experienced in the air blowing process. This was repeated three times and the results were compared with values obtained by the calculation procedure just described. Agreement within 4 per cent was obtained. This calculation, along with heat loss calibration and flowmeter and oxygen analyzer calibrations can be found in Appendix E.

#### F. Calculation of Oxygen Consumed

The total number of moles of oxygen consumed during an incremental reaction period can be determined by numerically integrating equation (16).

$$G = \frac{1}{32} \int_t^{t+\Delta t} (0.209 F_a - Y_O F_O) dt \quad (16)$$

where

$G$  = Oxygen reacted, lb. moles

$Y_O$  = Exit gas oxygen concentration, mass fraction

The heat of reaction is then obtained simply by dividing the negative of the heat generated by the number of moles of oxygen reacted.

$$\Delta H = - \frac{Q \times 10^{-3}}{1.8 G} \quad (17)$$

where

$$\Delta H = \text{Heat of reaction, kcal. gm. mole}^{-1}$$

The heat of reaction of the sulphurization of asphalt is obtained by dividing the negative of the heat generated by the number of moles of sulphur reacted.

A sample calculation of one particular heat of reaction value for the air blowing process and one heat of reaction value for the sulphurization process is included in Appendix G.

## CHAPTER V

### RESULTS

#### A. Air Blowing

The individual results obtained for the heat of reaction of air blowing asphalt are reported in Tables 2 and 3. All values are reported in kilocalories per gram mole of oxygen consumed.

TABLE 2

HEAT OF REACTION OF AIR BLOWING ASPHALT, TEMPERATURE 460 - 475 °F.

Asphalt	Heat of Reaction, kcal./gm. mole		
	East Texas Asphaltic Residuum S-62-2	Gulf Coast Naphthenic Residuum S-62-3	West Texas New Mexico Residuum S-63-3
Softening Point 70 - 100 °F.		-64.5 -60.9	
Softening Point 100 - 130 °F.	-73.2 -71.2	-64.5 -62.7	-68.5 -67.8
Softening Point 130 - 180 °F.	-71.0 -71.5	-65.9 -61.4	-71.3 -67.3
Softening Point 180 - 250 °F.	-74.0 -71.9	-57.0 -65.5	-69.3 -72.8

TABLE 3

HEAT OF REACTION OF AIR BLOWING ASPHALT, TEMPERATURE 535 - 550 °F.

Asphalt	Heat of Reaction, kcal./gm. mole		
	East Texas Asphaltic Residuum S-62-2	Gulf Coast Naphthenic Residuum S-62-3	West Texas New Mexico Residuum S-63-3
Softening Point 70 - 100 °F.		-61.1 -61.3	
Softening Point 100 - 130 °F.	-67.8 -66.4	-60.2 -60.1	-67.4 -68.1
Softening Point 130 - 180 °F.	-64.6 -65.8	-60.0 -63.3	-69.9 -68.7
Softening Point 180 - 250 °F.	-62.9 -66.6	-63.7 -60.2	-68.5 -67.8

A factorial analysis of variance was calculated for these data, excluding the softening point range 70 to 100 °F. The statistical data are reported in Appendix H. The analysis of variance of the air blowing reaction is presented as Table 4.

TABLE 4

## ANALYSIS OF VARIANCE OF ASPHALT AIR BLOWING RESULTS

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Blocks	1	0.0100	0.0100	0.002
Asphalt, A	2	379.5116	189.7558	36.703 **
Softening Point, B	2	0.0116	0.0058	0.001
Temperature, C	1	83.4117	83.4117	6.134 *
AB Interaction	4	12.6218	3.1554	0.654
AC Interaction	2	52.5407	26.2704	5.081 *
BC Interaction	2	1.3033	0.6516	0.136
ABC Interaction	4	17.5593	4.3898	0.849
Error	17	87.8900	5.1700	
Total	35	634.8600		

The single asterisk on the value of F in the analysis of variance means that the F is significant at the 95 per cent confidence limit and the double asterisk shows significance at the 99 per cent confidence limit.

The most apparent result of the analysis of variance is the highly significant F due to the effect of asphalt showing that the heat of reaction of air blowing asphalt differs for asphalts of different composition, a difference that is significant at the 99 per cent confidence limit. The significant F reported for the effect of temperature means that a change of temperature of the air blowing process modifies the heat of reaction. The fact that the F for the effect of softening point is not significant shows that

the heat of reaction does not significantly change as the air blowing reaction proceeds.

The significant F reported for AC or asphalt-temperature interaction means that the difference in heat of reaction due to temperature difference is not the same for all asphalts or, conversely, it means that the difference in the heat of reaction of different asphalts is not the same at different temperatures. The other interactions, asphalt-softening point, temperature-softening point, and asphalt-temperature-softening point, are not significant.

#### B. Catalytic Air Blowing

The individual results obtained for the heat of reaction of catalytic air blowing the Gulf Coast naphthenic residuum, S-62-3, with 2 per cent catalyst are reported in Table 5 along with a standard, the heat of reaction of air blowing S-62-3 from its initial softening point of 70 °F. to a softening point of 130 °F. Again the values are reported in kilocalories per gram mole of oxygen reacting.

By means of an analysis of variance of these data, which is reported in Appendix H, an error mean square of 2.89 is obtained. Dunnett's (23) procedure is applied and a Dunnett difference is calculated at both the 95 and 99 confidence limits by equation (18), which is recommended by Steel and Torrie (99) for use with an unequal number of replications.

TABLE 5

## HEAT OF REACTION OF CATALYTIC AIR BLOWING ASPHALT

	Heat of Reaction, kilocalories/gram mole		
	No Catalyst	Aluminum Chloride	Phosphorus Pentoxide
	-64.5	-71.0	-63.3
	-61.8	-71.1	-60.4
	-60.7		
	-60.7		
Mean	-61.9	-71.0	-61.8

$$\delta = \tau \sqrt{s \left[ \frac{1}{p} + \frac{1}{q} \right]} \quad (18)$$

where

$\delta$  = Dunnett's difference

$\tau$  = Dunnett's t

s = Error mean square

p = Replications with standard

q = Replications with comparison

The value of Dunnett's t for five degrees of freedom is 2.44 at the 95 per cent confidence limit and 4.21 at the 99 per cent confidence limit, which results in Dunnett differences of 3.5 and 6.0 at the 95 and 99 per cent confidence levels, respectively. From Table 5 it can be seen that the means of the standard, straight air blowing with no catalyst, and the comparison with phosphorus pentoxide do not differ by more than 3.5, and so their difference is not significant and it is concluded that the use of phosphorus pentoxide as a catalyst has no significant effect on the magnitude of the heat of reaction of air blowing asphalt. However the mean of the standard and the mean of the comparison of catalytic air blowing with aluminum chloride differ by more than 6.0, hence the difference is highly significant and it is concluded that the use of aluminum chloride has a highly significant effect on the magnitude of the heat of reaction.

### C. Sulphurization

The individual results obtained for the heat of reaction in the asphalt sulphurization process are reported in Table 6. All values are reported in kilocalories per gram mole of sulphur reacting.

TABLE 6

#### HEAT OF REACTION OF SULPHURIZING ASPHALT

Heat of Reaction, kilocalories/gram mole			
	East Texas Asphaltic Residuum S-62-3	Gulf Coast Naphthenic Residuum S-62-3	West Texas New Mexico Residuum S-63-3
	+11.2	+8.3	+8.6
	+14.5	+6.6	+9.4
	+12.0	+7.5	+8.3
	+11.1	+8.0	+8.8
		+10.4	+10.3
			+8.4
Mean	+12.2	+8.2	+9.0

An analysis of variance of these data, the statistical data for which appear in Appendix H, is reported as Table 7.

TABLE 7

## ANALYSIS OF VARIANCE OF ASPHALT SULPHURIZATION RESULTS

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Among	2	41.702	20.851	13.6 **
Within	12	18.365	1.530	
Total	14	60.067		

The highly significant F obtained indicates that the heat of reaction of sulphurizing asphalt is significantly different with different types of asphalts at the 99 per cent confidence limit.

## CHAPTER VI

### ANALYSIS OF RESULTS

#### A. Air Blowing

The highly significant difference in the value of the heat of reaction for different asphalts demonstrates that different types of reactions do indeed play a more important role in certain types of asphalts. The lack of significance in the effect of softening point seems to indicate that the same types of reactions occur throughout the blowing period of a given asphalt, although this cannot be stated conclusively, since compensating changes could occur in which the heat of reaction per mole of oxygen consumed would not change. The significant difference in the heat of reaction for operation at different temperature levels implies that different reactions do have a greater importance at different reaction temperatures, if the effect of change in heat capacity may be ruled out, which is not an unreasonable assumption over the moderate temperature range considered. The significant asphalt-temperature interaction indicates that the response to change in temperature is not the same for all asphalts. This becomes readily apparent from an analysis of Table 8, which is a condensation of the air blowing results.

TABLE 8

## SUMMARY OF AIR BLOWING RESULTS

Asphalt	Heat of Reaction, kcal./gm. mole	
	Temperature 460 - 475 °F.	Temperature 535 - 550 °F.
East Texas Residuum, S-62-2	-72.1	-65.7
Gulf Coast Naphthenic, S-62-3	-62.8	-61.2
West Texas-New Mexico, S-63-3	-69.5	-69.0

Examination of Table 8 reveals that the temperature effect is experienced almost entirely by one asphalt alone, S-62-3, accounting for the significant asphalt-temperature interaction.

The heats of reaction for the various types of reactions that have been postulated to take place during air blowing are presented in Table 9. These values were determined by applying the general principle that the heat of formation of a chemical bond is a constant independent of the remaining structure of the molecule. Pauling (78) has shown that this assumption agrees quite well with experimental values. The calculation for each of these reactions is shown in Appendix F. The values are reported in kilocalories per gram mole of oxygen reacting with water as a gaseous product.

TABLE 9

## CALCULATED HEAT OF REACTION VALUES FOR PROPOSED AIR BLOWING REACTIONS

Proposed Reaction	Heat of Reaction, kcal./gm. mole
Dehydrogenation of single bond to form double bond	-55.2
Aromatization of naphthenic ring to aromatic ring	-83.0
Direct carbon-carbon bond formation	-93.9
Formation of oxygen containing functional groups	
Ketone on side chain	-90.2
Ketone with naphthenic ring rupture	-95.2
Carboxylic acid	-102.7
Hydroxyl group	-99.0
Anhydride	-85.7
Ester	-93.2
Ether	-77.2
Decarboxylation	+4.8 of CO <sub>2</sub> (checked)

A correspondence between the calculated heat of reaction values shown in Table 9 and the experimental values shown in Table 8 does not in itself justify the proposal of a mechanism for the air blowing reaction because the combination of various reactions occurring in different proportions could result in almost any over-all heat of reaction value. However, such a correspondence can provide corroborating evidence that a mechanism proposed on the basis of additional evidence does indeed occur. Conversely, the lack of a correspondence

in an experimental heat of reaction value and the calculated value of a proposed reaction mechanism provides evidence that the proposed mechanism may not be as important as had been postulated.

It is seen that ester formation and carbon-carbon linkage have nearly the same heat of reaction, which means that no information will be revealed concerning which of these two postulated polymerization linkages may be favored under certain conditions. It is interesting to note that the only proposed reaction with a less negative value of the heat of reaction than the experimental results is the dehydrogenation of single bonds to form double bonds. Furthermore the magnitude of the experimental results, approximately -65 kilocalories per gram mole of oxygen reacted, is somewhat closer to the value of the dehydrogenation reaction, -55 kilocalories per gram mole, than it is to the value of the polymerization reactions or functional group formations, about -90 kilocalories per gram mole. This implies that dehydrogenation of the asphalt is the principal reaction taking place during air blowing, accounting for over half of the oxygen reacted.

According to Gun (37) the aliphatic chains are not dehydrogenated during air blowing, although naphthenic rings may be dehydrogenated. If this is the case, then it appears that only one or possibly two of the bonds in the naphthenic ring are dehydrogenated. Dehydrogenation of a naphthenic structure to produce an aromatic structure

has a more negative heat of reaction than dehydrogenation of only one or two bonds because of resonance in the aromatic rings. Since this value, - 83.0 kilocalories per gram mole, is higher than any of the experimental values, the results indicate that aromatization does not occur to a very great extent in air blowing.

Because the formation of an oxygen group (except ether and anhydride groups) produces a heat of reaction more negative than -90 kilocalories per gram mole, and because these types of reactions must occur because of the increase in the oxygen content of the asphalt, then it must follow that reactions with a rather large negative heat of reaction that do not contribute oxygen to the asphalt structure take place to a rather limited extent.

The fact that ether formation results in a less negative heat of reaction than other oxygen group formation, which is more in agreement with the experimental results, lends support to the theory that ether bridges are formed in the air blowing reaction, although the experimental results certainly do not justify a definite statement on this matter.

In addition it is noted that the heat of reaction values of asphalt S-62-3, the Gulf Coast naphthenic, are less negative than those for the other two, indicating that dehydrogenation may be even more important in this asphalt than the others. This is not surprising because the Schweyer-Chipley (94) analysis of S-62-3 shows that it has the highest naphthenic + paraffinic fraction and

the Traxler-Schweyer (103) analysis shows that it has the highest saturate fraction, hence S-62-3 has more saturated bonds available for dehydrogenation. It was also noted qualitatively that this asphalt consumes more oxygen with a smaller change in flow properties than the other two, which might be because dehydrogenation would have less effect on the viscosity of the asphalt than polymerization.

#### B. Temperature Effect

The finding that the heat of reaction values are slightly less negative in the high temperature range of 535 to 550 °F. than the low range of 460 to 475 °F. can be attributed to the decarboxylation that has been proposed by Goppel and Knotnerus (34) to occur at higher temperatures. Oxygen analyses of air blown samples of S-62-3 obtained from runs at different temperatures shows that at a temperature of 535 to 550 °F. when 0.060 pound moles of oxygen react with asphalt, 0.018 pound moles are retained by the asphalt, while at a temperature of 460 to 475 °F., 0.084 pound moles of oxygen must react before the same quantity is retained by the asphalt, or about 40 per cent more, indicating that a greater percentage of the reacting oxygen becomes chemically bound in the asphalt at lower temperatures. This confirms the statement of Goppel and Knotnerus (34) proposing decarboxylation and the preferential formation of carbon-carbon bonds over ester bonds in high temperature polymerization.

The decarboxylation to form carbon dioxide would result in a less negative heat of reaction of about 4.8 kilocalories per gram mole weighted by the fraction of oxygen actually leaving the system as carbon dioxide.

The significant asphalt-temperature interaction due to the behavior of asphalt S-62-2, the East Texas asphaltic residuum, is more difficult to analyze. The effect is obviously not entirely due to decarboxylation because the effect is larger than 4.8 kilocalories per gram mole and decarboxylation is a reaction of relatively minor importance. This temperature effect of S-62-2 was also noticed by Ariet (6), who reports that this particular asphalt has the highest energy of activation in the air blowing reaction of six asphalts that he studied, although he gives no explanation for its higher value. The Traxler-Schweyer (103) analysis of S-62-2 reveals that it has the highest asphaltic content of the three asphalts studied and the air blowing kinetic rate was shown to be dependent upon the asphaltic fraction concentration at a temperature of 550 °F. (6). It has also been reported by Goppel and Knotnerus (34) that aromatic asphalts are more susceptible to functional oxygen group formation in air blowing than other types. The asphaltic content of S-62-2 may be related to a high concentration of aromatic compounds,

based on the data of Romberg, Nesmith, and Traxler (86). Therefore the decarboxylation effect on the heat of reaction would be expected more for S-62-2 and in addition Ariet's (6) results indicate that the kinetics constants of asphalts with a high asphaltic fraction content are more susceptible to temperature than the constants for other asphalts. The combination of these two phenomena could very likely be responsible for the significant asphalt-temperature interaction.

### C. Catalytic Air Blowing

The results obtained for the heat of reaction of catalytic air blowing asphalt S-62-3, the Gulf Coast naphthenic residuum, are summarized in Table 10.

TABLE 10

#### SUMMARY OF CATALYTIC AIR BLOWING RESULTS

Catalyst	Heat of Reaction, kcal./gm. mole
None	-61.9
Aluminum Chloride	-71.0
Phosphorus Pentoxide	-61.8

The observation that the difference in the heat of reaction of catalytic air blowing with phosphorus pentoxide and air blowing with no catalyst was not significant yields little information concerning the effect of this catalyst. Since Hoiberg (44) reports that  $P_2O_5$  increases the penetration by 147 per cent and the blowing time by 6 per cent, it obviously cannot be concluded that the catalyst has no effect on the reaction. However, because the magnitude of the heat of reaction is not altered significantly by the addition of  $P_2O_5$ , it is improbable that a reaction of the type with a low heat of reaction is preferentially accelerated over a reaction with a higher heat of reaction or vice versa. An oxygen analysis of a sample of  $P_2O_5$  blown asphalt shows that only about 7 per cent of the reacting oxygen is bound in the asphalt as compared with over 20 per cent in air blowing without a catalyst. This point, in addition to the great change in the softening point-penetration curve shown by Hoiberg (44) could indicate that the formation of oxygen containing groups is preferentially retarded in favor of a polymerization reaction, especially by direct carbon-carbon bond linkage. Since the magnitude of the heats of reaction of these two reactions are nearly identical, such preferential catalysis would not be revealed by a change in the magnitude of the heat of reaction. Once again, however, the possibility of compensations produced by a complex of reactions makes it difficult to state anything about this catalyst conclusively.

The highly significant difference in the heat of reaction obtained with the use of aluminum chloride, which decreases the magnitude of the heat of reaction from -62 to -71 kilocalories per gram mole indicates that the types of reactions with more negative heats of reactions are preferentially accelerated at the expense of those with less negative heats of reaction. Hoiberg (44) reports that the softening point-penetration curve is altered little by the use of this catalyst, which would indicate that the polymerization reactions are not affected. An oxygen analysis of a sample taken during air blowing with  $\text{AlCl}_3$  reveals that 31 per cent of the reacting oxygen is retained by the asphalt as compared with about 24 per cent during comparable air blowing with no catalyst. It is postulated, therefore, that a preferential acceleration of oxygen group formation which has a heat of reaction of about -90 to -100 kilocalories per gram mole and a retardation of the dehydrogenation reaction which has a heat of reaction of -55 kilocalories per gram mole is the probable effect of aluminum chloride since this would result in a more negative over-all heat of reaction.

#### D. Sulphurization of Asphalt

The highly significant difference in the heat of reaction of the asphalt-sulphur reaction due to the type of asphalt demonstrates that certain reactions play a more important role with different asphalts in this process as well as in the air blowing

process. The results obtained for the heat of reaction for the asphalt-sulphur reaction are summarized in Table 11.

TABLE 11

## SUMMARY OF SULPHURIZATION RESULTS

Asphalt	Heat of Reaction, kcal./gm. mole
East Texas Residuum, S-62-2	+12.2
Gulf Coast Naphthenic, S-62-3	+8.2
West Texas-New Mexico, S-63-3	+9.0

The heats of reactions for the various types of asphalt-sulphur reactions that have been proposed to take place are given in Table 12. The same assumptions used in the calculations of the air blowing reactions were applied in this case with the exception that hydrogen sulphide rather than water was produced. The individual calculations are presented in Appendix F. The values are reported in kilocalories per gram mole of sulphur reacting.

It is immediately clear that the experimental results are lower than most of the heat of reaction values listed in Table 12 and so those reactions with a relatively high heat of reaction must take place to a very limited extent. The dehydrogenation reaction, which was proposed to be an important reaction in the air blowing

TABLE 12

CALCULATED HEAT OF REACTION VALUES FOR PROPOSED SULPHURIZATION REACTIONS

Proposed Reaction	Heat of Reaction, kcal./gm. mole
Dehydrogenation of aliphatic bond to form olefin	+24.8
Aromatization of naphthenic ring to aromatic ring	+10.9
Direct carbon-carbon bond formation	+6.4
Thiol formation	+10.4
Sulphide formation	+10.1
Closure of aliphatic chain to thiophene type ring	+25.9
Dehydrogenation followed by sulphide linkage alpha to double bond	+17.4
Dimerization reactions of alkyl aromatics	
Aliphatic linkage	+6.4
Olefinic linkage	+15.6
Thiophene type linkage	+19.1

process has a heat of reaction of 24.9 kilocalories per gram mole with sulphur, which is almost prohibitively high. This is not unexpected considering Brooks' (10) report that olefins are very reactive with sulphur. Furthermore, the Gulf Coast naphthenic asphalt, S-62-3, which is expected to have the most aliphatic bonds available for dehydrogenation, has the lowest heat of reaction of the three asphalts studied. If dehydrogenation of paraffins did occur, it would be expected that the high heat of reaction of this reaction would make the experimental value for S-62-3 higher than the other two.

Although the evidence indicates that dehydrogenation of aliphatics does not occur, it is quite likely that the dehydrogenation of naphthenic rings to aromatic structures, as suggested by the work of Ruzicka and Meyer (89) and Ruzicka, Meyer, and Mintazzini (90), does take place. The heat of reaction for this reaction, 10.4 kilocalories per gram mole, is in the range of the experimental results. Pryor (83) reports that this reaction takes place with many naphthenic structures since the aromatic structures formed are not further reactive with sulphur as are the olefins. The air blowing process heat of reaction results indicated that the dehydrogenation of one or two bonds of a naphthenic ring is one of the major reactions. In the sulphurization process, it is likely that the same type of reaction takes place, except that the high reactivity of the sulphur results in all three bonds of the naphthenic ring being dehydrogenated.

The heats of reaction in the formation of thiols and sulphides are in the order of magnitude of the experimental results, but Tucker's (104) finding that only about 15 per cent of the sulphur reacting with the asphalt remains chemically bound in the asphalt prohibits these reactions from playing more than a minor role. Tucker has found, however, that the sulphur content of the asphaltenes increases during sulphurization, especially with low sulphur asphalts. This contrasts with Gun's (36) finding that the oxygen content of asphaltenes decreases during air blowing and indicates that polymerization by sulphur linkage may be more important in the asphalt-sulphur reaction than polymerization by oxygen linkage is in the air blowing reaction. The magnitude of the heat of reaction values about 10 kilocalories per gram mole indicates that this polymerization may indeed occur by the formation of sulphides.

The fact that the closure of an aliphatic chain to form a thiophene type ring has a heat of reaction value much higher than the experimental results indicates that this reaction must take place to a rather limited extent, if at all. Tucker's (104) results bear this out; he has found that none of the reacting sulphur becomes bound in the paraffinic + naphthenic fraction obtained by the Schweyer-Chipley analysis method (94).

Polymerization by dehydrogenation followed by sulphide cross linking alpha to the double bond has a heat of reaction of about 17 kilocalories per gram mole of sulphur reacting, which is

somewhat higher than the experimental results of about 12, 9, and 8 kilocalories per gram mole for S-62-3, S-62-3, and S-63-3, respectively, but it is a very likely possibility nevertheless because the temperature of the sulphurization process is favorable for this reaction, according to Westlake (107). The formation of direct carbon-carbon bonds must also be considered very probable because it is the only reaction with a lower heat of reaction than all of the experimental results. These two reactions occurring simultaneously would have an over-all heat of reaction with a magnitude in the range of the experimental results.

The reason for the highly significant difference in the magnitude of the heats of reaction for the three asphalts is difficult to determine. The most naphthenic of the three by component analysis, the Gulf Coast naphthenic, S-62-3, has the lowest heat of reaction, 8.2 kilocalories per gram mole, while the most asphaltic, the East Texas, S-62-2, has the highest, 12.2. This implies that naphthenic asphalts are more susceptible to polymerization by carbon-carbon bond linkage and that aromatic asphalts are more susceptible to polymerization by sulphide linkage. Another explanation could be that Horton's (48) dimerization reactions of alkyl aromatics take place to a certain extent. Olefinic linkage or thiophene type linkage by aromatic structures would be expected to result in an elevated heat of reaction value for the more aromatic type asphalts.

It should be emphasized that the purpose of this research was to measure and report heat of reaction data for the processing of asphalts. Attempts to explain mechanism from the values of the heat of reaction are valid only when supplemented by the findings of Ariet (6), Tucker (104), and Busot (13), as well as other investigators.

## CHAPTER VII

### CONCLUSIONS

The following conclusions concerning the heat of reaction of processing asphalt can be drawn.

1. The asphalt air blowing reaction was found to be exothermic with a heat of reaction varying between -61 and -72 kilocalories per gram mole of oxygen reacted, depending upon the type of asphalt and the blowing temperature. The effect of the type of asphalt was significant at the 99 per cent confidence limit and the effect of temperature was significant at the 95 per cent confidence limit. The extent of completion of the air blowing process was found to have no effect on the magnitude of the heat of reaction.

2. The results indicated that dehydrogenation of single bonds to double bonds, especially the single bonds in naphthenic rings, may account for over half of the oxygen consumed. The heat of reaction of one asphalt, a Gulf Coast naphthenic residuum, S-62-3, indicated that dehydrogenation is more prominent in this asphalt than the other two studied.

3. The heat of reaction of another asphalt, an East Texas asphaltic residuum, S-62-2, was more sensitive to temperature than the other two. This was attributed to its possible higher aromatic composition.

4. Air blowing with one catalyst, phosphorus pentoxide, proved to have no effect on the magnitude of the heat of reaction, but air blowing with another, aluminum chloride, decreased the magnitude of the heat of reaction by 9 kilocalories per gram mole, a difference that was significant at the 99 per cent confidence limit. This was attributed to the catalyst's preferential acceleration of reactions forming oxygen containing groups at the expense of dehydrogenation reactions.

5. The asphalt sulphurization process was found to be endothermic with a heat of reaction varying between 8 to 12 kilocalories per gram mole of sulphur reacted depending upon the type of asphalt, which was significant at the 99 per cent confidence limit.

6. The results indicated that polymerization in the asphalt-sulphur reaction may take place by both sulphide linkage and by carbon linkage. Sulphur linkage was postulated to be more important in this reaction than oxygen linkage is in air blowing polymerization.

7. Dehydrogenation of naphthenic rings was postulated to take place in the sulphurization process as well as the air blowing process; however with sulphur all three bonds of the naphthenic rings may be dehydrogenated resulting in an aromatic structure. The formation of stable olefinic double bonds was found to be unlikely.

8. It was concluded that oxygen and sulphur both dehydrogenate and polymerize asphalt. The indications for the differences in these two reactants lies principally in that oxygen dehydrogenates

only one or two naphthenic bonds while sulphur dehydrogenates all three, and that polymerization is accomplished more by sulphur linkage in the sulphurization process than by oxygen linkage in the air blowing process.

## APPENDIX A

### DRAWINGS OF EQUIPMENT

## APPENDICES

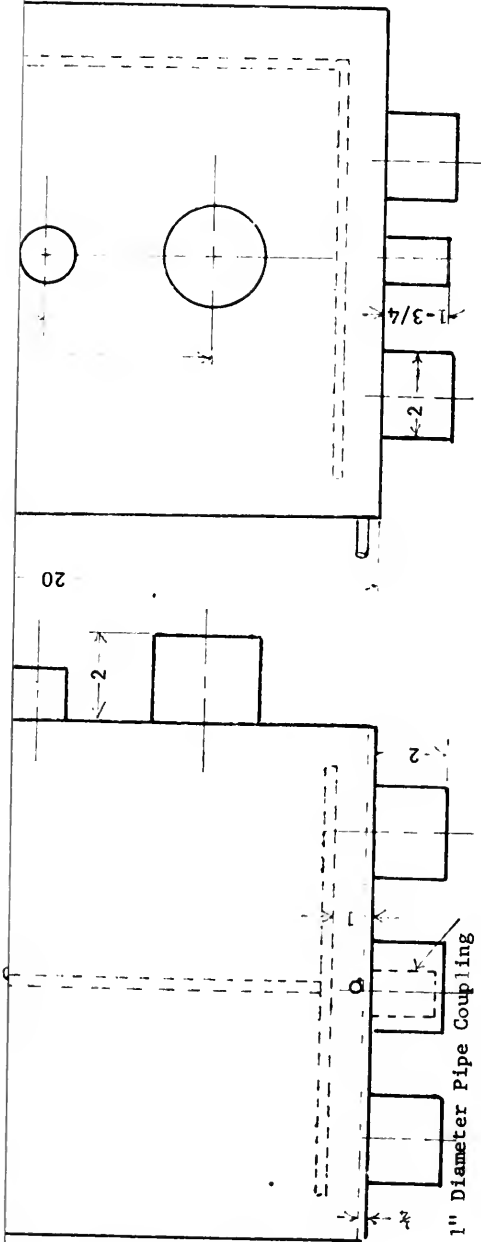
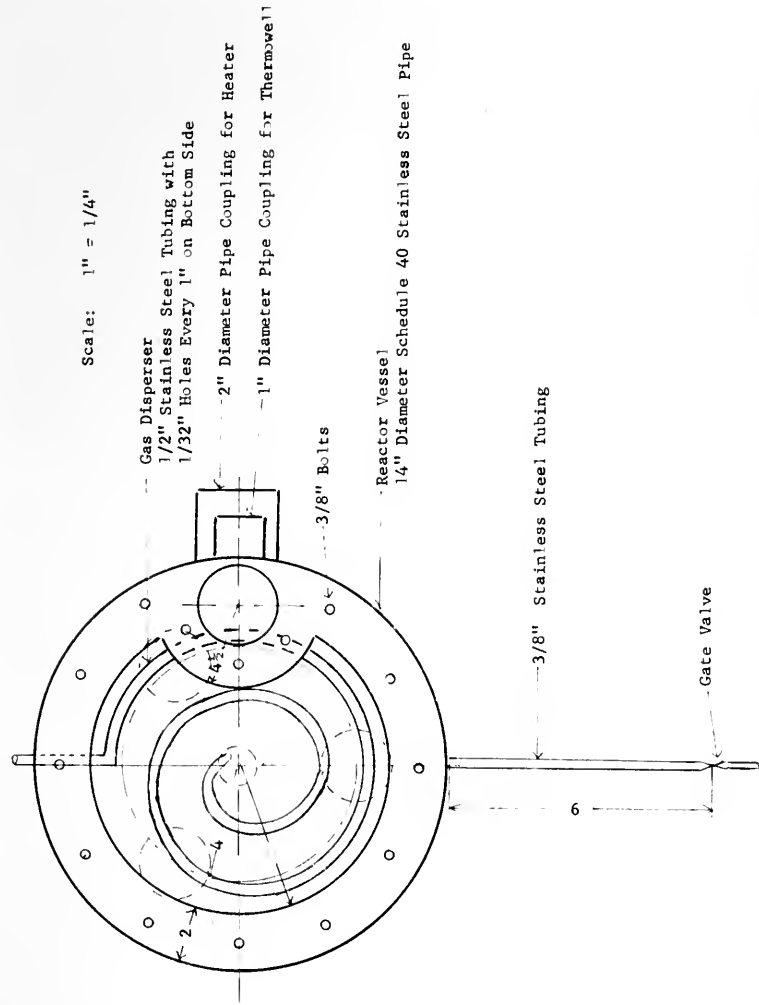


Figure 4. Experimental Reactor





2" Diameter Pipe Coupling

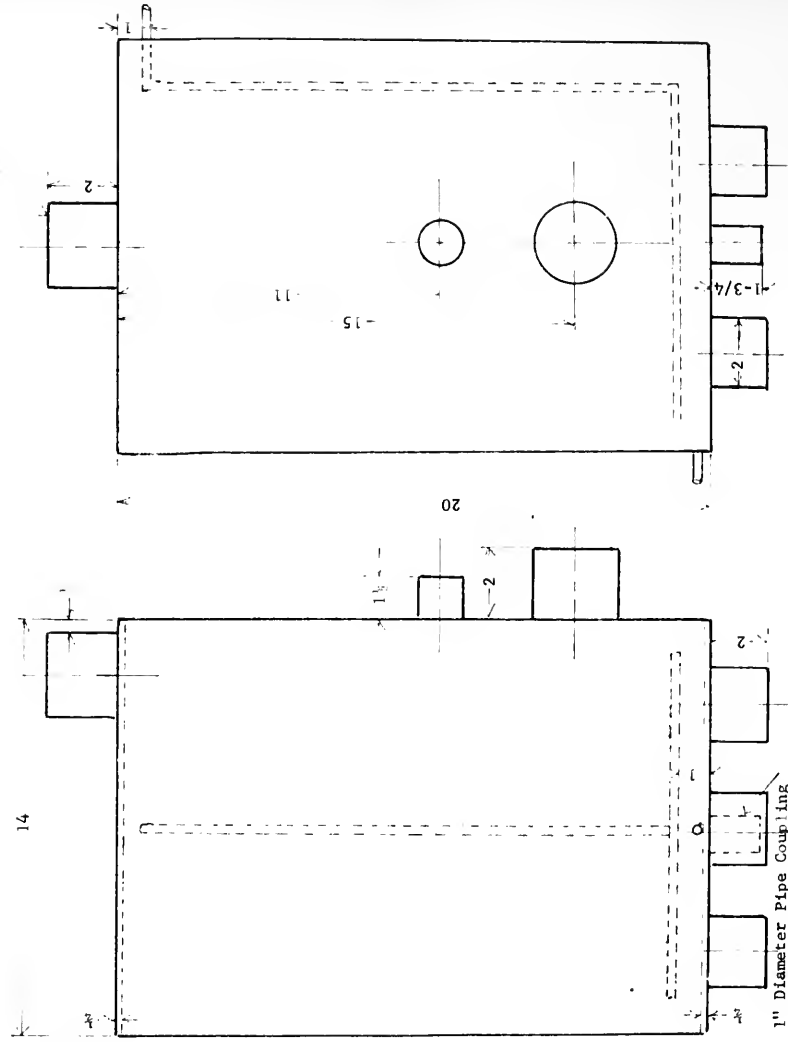
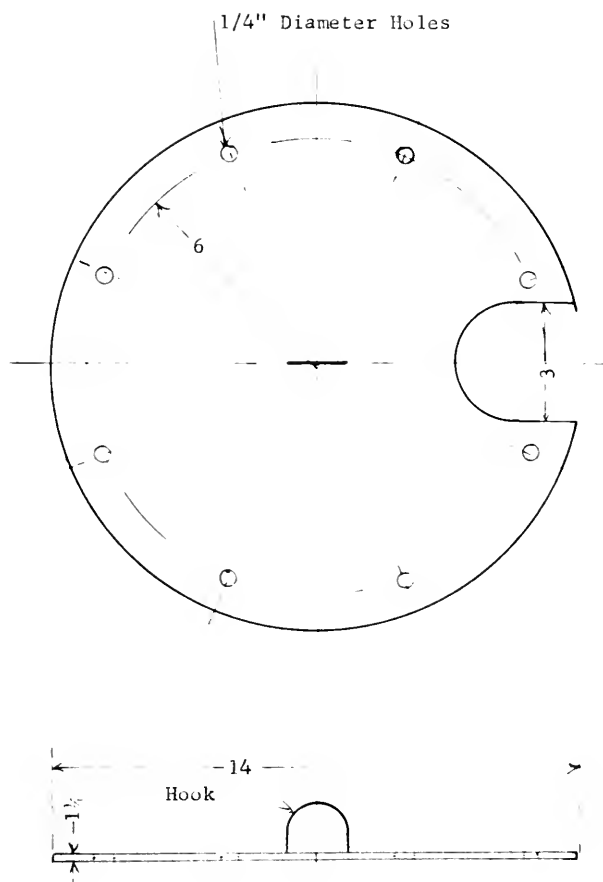


Figure 4. Experimental Reactor



Scale: 1" = 1/4"

Figure 5. Reactor Cover

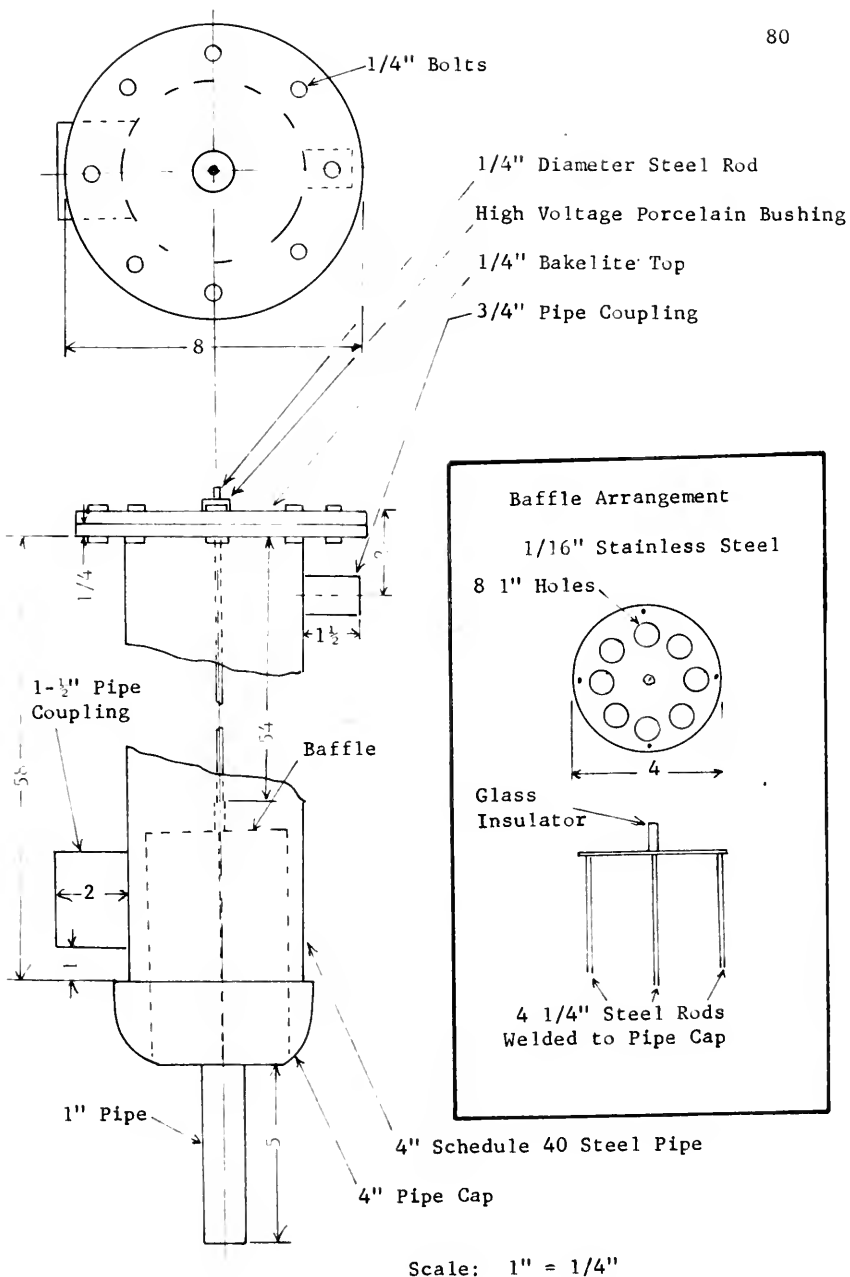


Figure 6. Electrostatic Precipitator

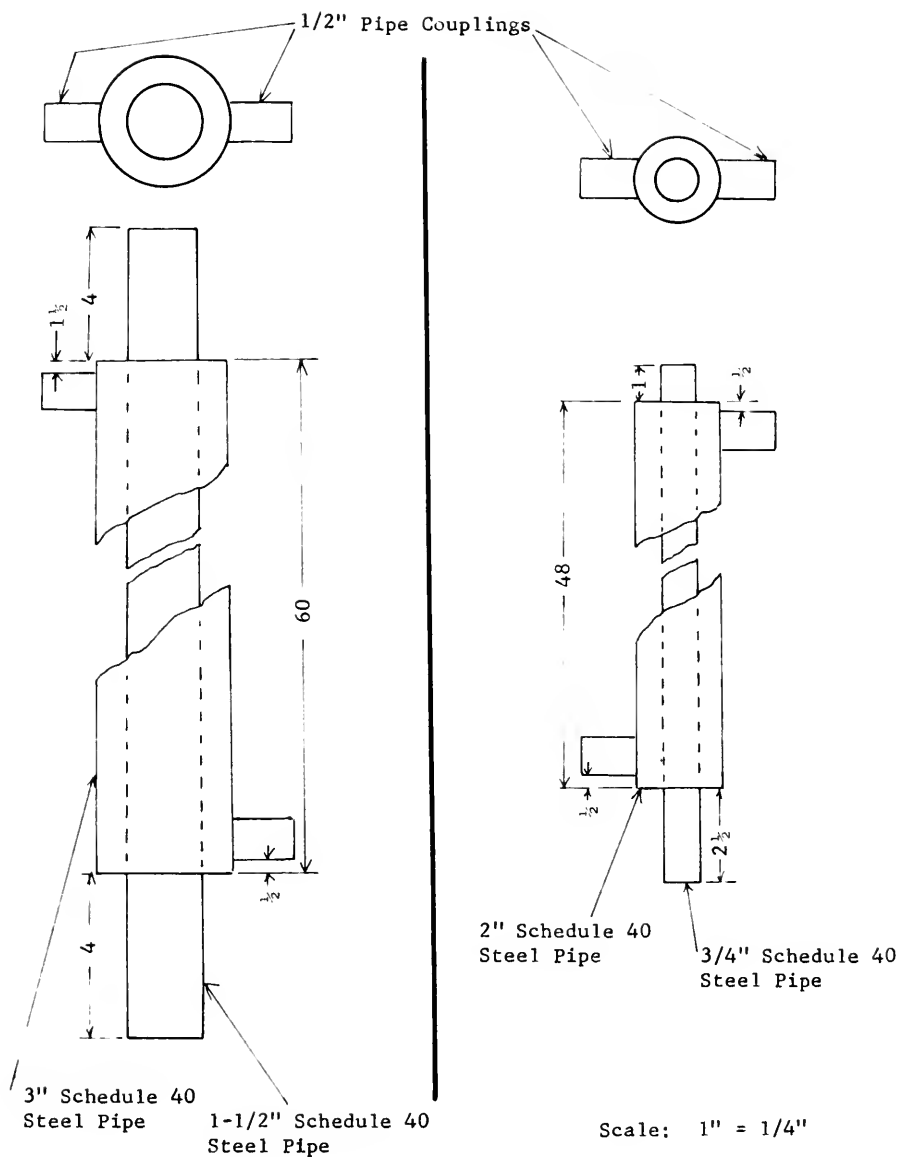


Figure 7. Double Pipe Heat Exchangers

Scale: 1" = 1/4"

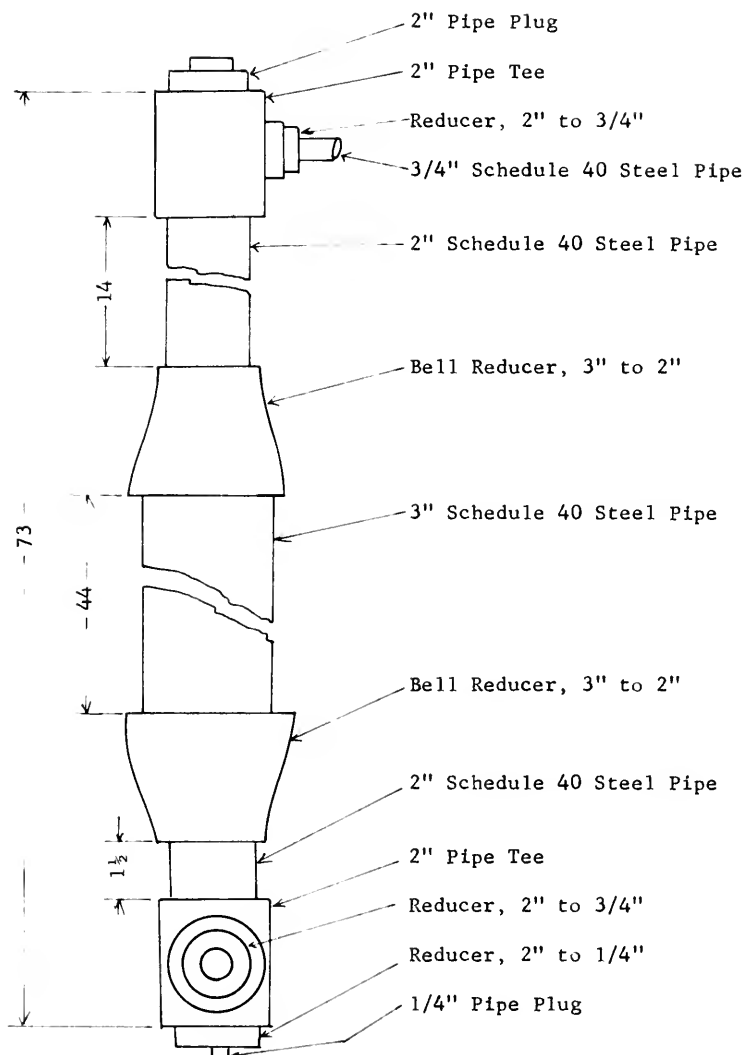


Figure 8. Packed Column

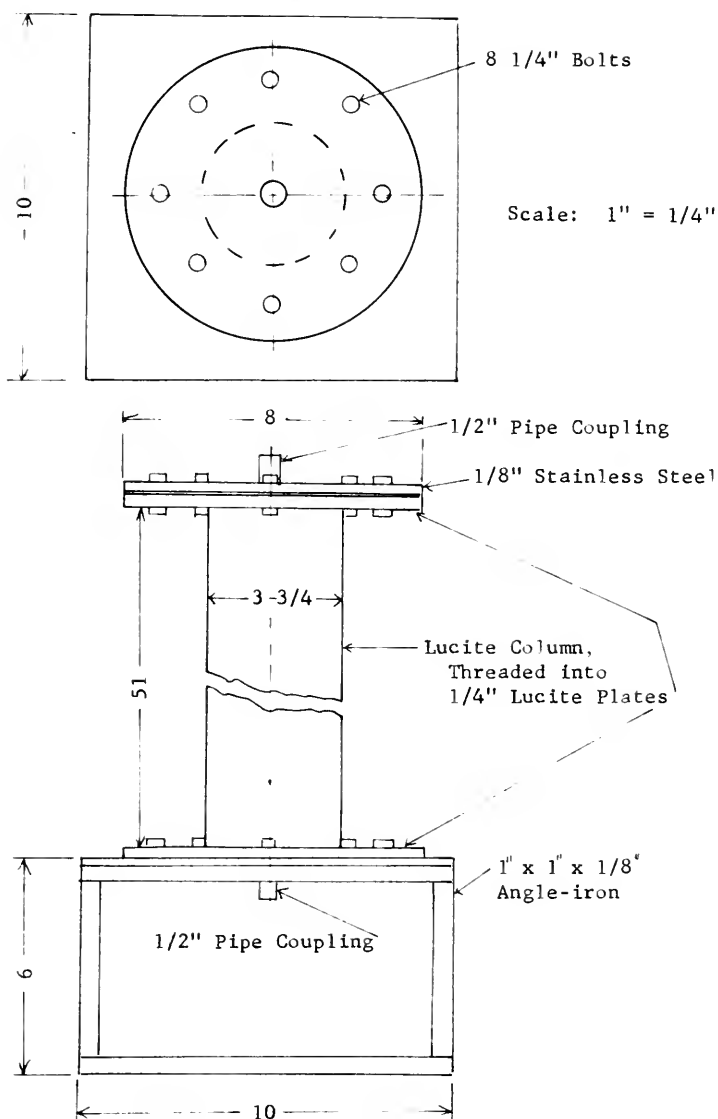


Figure 9. Drying Column





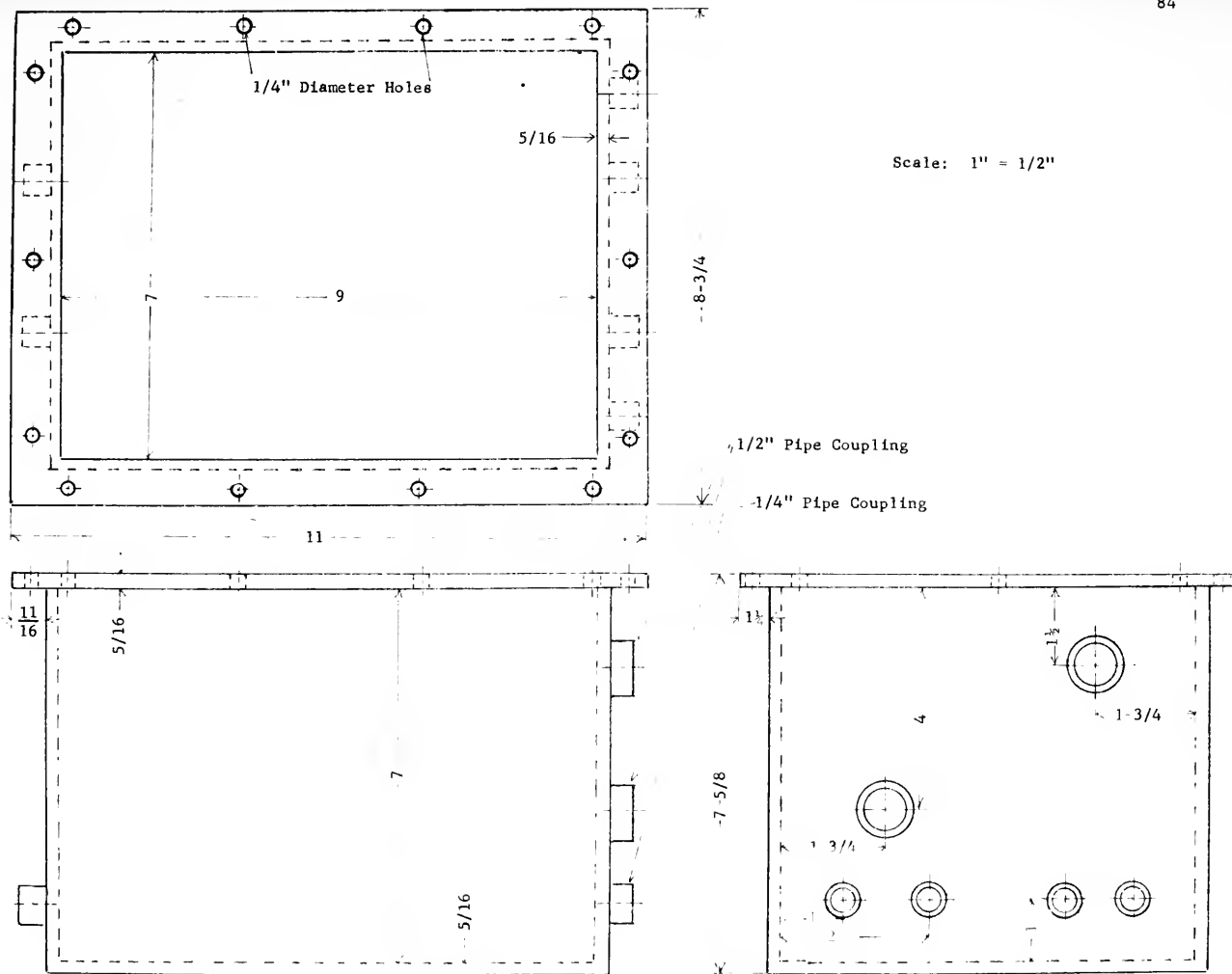
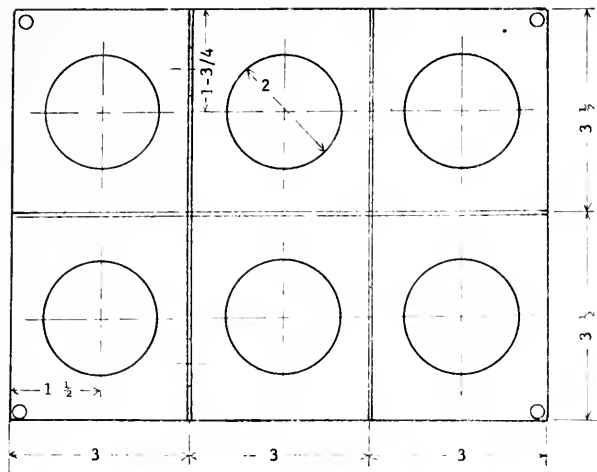


Figure 10. Gas Preheater.

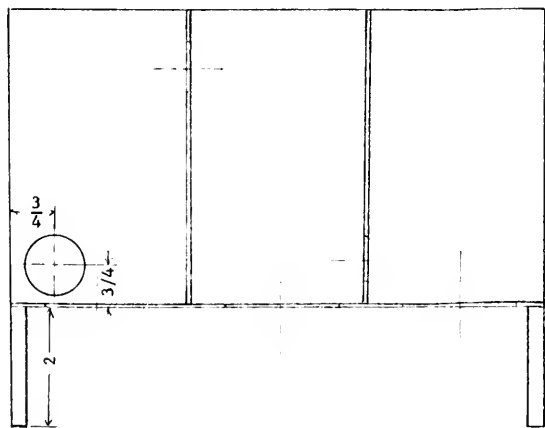




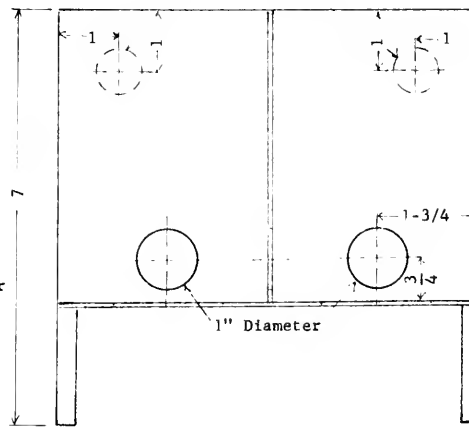
Scale: 1" = 1/2"

1/16" Steel Sheet

3/4" Diameter

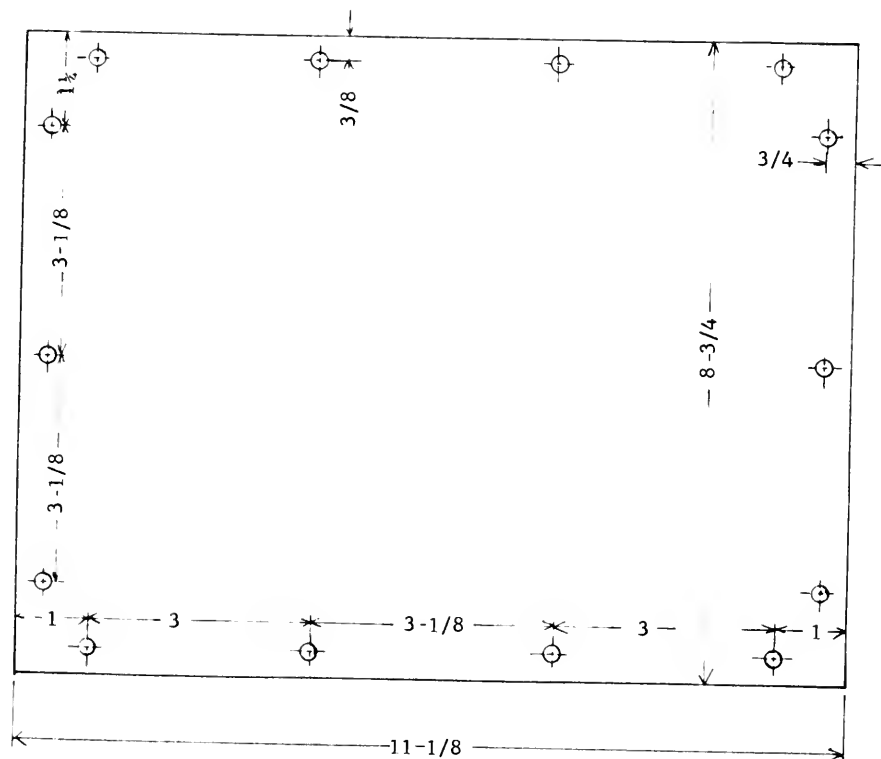


$\frac{1}{2}$ " Diameter



1" Diameter

Figure 11. Preheater Baffles



All Holes 1/4" Diameter

Scale: 1" = 1/2"

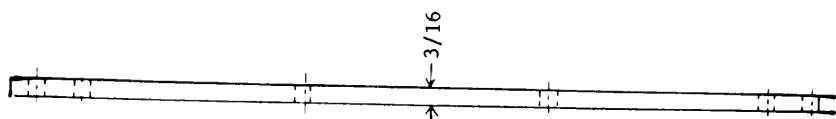


Figure 12. Preheater Cover



## APPENDIX B

### CALCULATION OF BOUNDARY CONDITION 2

The second boundary condition of equation (11) can be determined from a knowledge of the over-all heat transfer coefficients of the system. The over-all heat transfer coefficient appears in the equation

$$\Psi/S = \lambda (T_{R_{\alpha}} - T_{am}) \quad (19)$$

where

- $\lambda$  = Over-all heat transfer coefficient between reactor and ambient air,  $\text{BTU (linear ft.)}^{-1} \text{ } ^{\circ}\text{F.}^{-1} \text{ hr.}^{-1}$
- $\Psi$  = Quantity of heat transferred, BTU
- $S$  = Heat transfer area, linear ft. of reactor
- $T_{R_{\alpha}}$  = Reactor temperature,  $^{\circ}\text{F.}$
- $T_{am}$  = Ambient air temperature,  $^{\circ}\text{F.}$

A similar expression for the over-all heat transfer coefficient, which is due primarily to convection heat transfer, between the outside of the insulation and the ambient air can be written.

$$\Psi/S = \mu (T_{R_{\beta}} - T_{am}) \quad (20)$$

where

- $\mu$  = Over-all heat transfer coefficient between the outside of the insulation and ambient air,  $\text{BTU (linear ft.)}^{-1} \text{ } ^{\circ}\text{F.}^{-1} \text{ hr.}^{-1}$

$T_{R\theta}$  = Temperature of the outside of the insulation, °F.

For given values of reactor temperature, ambient air temperature, reactor diameter, and total thickness of insulation, the values of  $\psi/S$  and  $T_{R\theta}$  can be read directly from Table 13, which is reproduced from a more extensive table appearing in reference (50).

TABLE 13

## HEAT TRANSMISSION DATA OF THERMOBESTOS INSULATION

Pipe Diameter, inches	Pipe Temperature, ° F.	Ambient Air Temperature, ° F.	Insulation Thickness, inches	Outside Surface Temperature ° F.	Heat Transferred, BTU/linear ft. hr.
14	500	80	1 1/2	143	408
14	500	80	2	129	325
14	500	80	2 1/2	120	272
14	500	80	3	114	236
14	500	80	3 1/2	109	210
14	500	80	4	106	190
14	500	80	4 1/2	103	174
14	500	80	5	100	161
14	500	80	5 1/2	98	150
14	500	80	6	96	141

For a 14-inch reactor with 6 inches of insulation when  $T_{R\theta} = 500$  °F. and  $T_{am} = 80$  °F., then  $\psi/S = 141$  BTU per linear foot of 14-inch reactor per hour and  $T_{R\theta} = 96$  °F. Then

$$\lambda = \frac{141}{(500 - 80)} = 0.336$$

and

$$\mathcal{U} = \frac{141}{(96 - 80)} = 8.81$$

Assuming that the heat transfer coefficients are constant over the temperature range over which the reaction was carried out, and that  $\Psi/S$  is constant, which is true when  $\Psi/S$  is expressed in BTU per linear foot of 14-inch reactor per hour, then the following relation can be obtained by equating equations (19) and (20).

$$\lambda (T_{R_{\alpha}} - T_{am}) = \mathcal{U} (T_{R_{\beta}} - T_{am}) \quad (21)$$

or

$$T_{R_{\beta}} = 0.0382 (T_{R_{\alpha}} - T_{am}) + T_{am} \quad (22)$$

Since both the ambient air temperature and the reactor temperature are experimentally measured functions of time, it is quite simple to express  $T_{R_{\beta}}$  as a function of time,  $T = g(t)$ , by programming equation (22) to the IBM 709 computer with the input data  $T_{R_{\alpha}}$  and  $T_{am}$  at successive increments of time.

## APPENDIX C

### STABILITY OF THE FINITE DIFFERENCE EQUATION

The stability of a finite difference equation can be determined by the following theorem (69).

The five point difference equation

$$T_{m+1,n} - 2aT_{m,n} + b^2T_{m-1,n} = cT_{m,n+1} + dT_{m,n-1} \quad (23)$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are real constants with the boundary conditions

$$T_{0,n} = wT_{1,n} + u(n) \text{ at } m = 0, \text{ the initial boundary,}$$

$$T_{B,n} = yT_{B-1,n} + v(n) \text{ at } m = B, \text{ the final boundary,}$$

where  $w$ ,  $y$ ,  $u(n)$  and  $v(n)$  are either constants or function of time and additional arbitrary initial conditions at  $n = 0$  and  $n = 1$  (or merely at  $n = 0$  if  $d = 0$ ), is stable if, and only if, the following conditions are fulfilled.

1. The roots of the equation

$$D^2 + \frac{2}{c}(a - b \cos \alpha)D + d = 0 \quad (24)$$

cannot exceed unity in absolute value for any real value of  $\alpha$ .

2. Neither  $D = +1$  nor  $D = -1$  may be a repeated root of equation (24).

The five point difference equation corresponding to equation (23) is the following rearrangement of equation (14).

$$T_{m+1,n} + \frac{(N - 1/m - 2)}{(1 + 1/m)} T_{m,n} + \frac{1}{(1 + 1/m)} T_{m-1,n} = \frac{N}{(1 + 1/m)} T_{m,n+1} \quad (25)$$

where

$$N = \frac{C_i \rho (\Delta r)^2}{k (\Delta t)}$$

$$C_i = 0.28 \text{ BTU lb.}^{-1} \text{ } ^\circ\text{F.}^{-1}$$

$$k = 0.46 \text{ BTU } ^\circ\text{F.}^{-1} \text{ hr.}^{-1} \text{ ft.}^{-2} \text{ in.}$$

$$\rho = 11 \text{ lb. ft.}^{-3}$$

$$\Delta r = 1 \text{ in.}$$

$$\Delta t = 5 \text{ min.}$$

$$N = 6.7$$

$$m = r/\Delta r.$$

Obviously  $m$  is not a constant and so  $a$ ,  $b$ , and  $c$  are not constants, which violates one of the conditions of the theorem. However Mickley, Sherwood, and Reed (69) state that in the case of variable coefficients, if the equation is stable for all possible values of the variable, then it is reasonable to assume that the equation is stable, although this procedure cannot be guaranteed to be valid.

The coefficients in the five point difference equation are:

$$a = \frac{-(N - 1/m - 2)}{2(1 + 1/m)}$$

$$\begin{aligned}
 b &= \pm \sqrt{\frac{1}{(1 + 1/m)}} \\
 c &= \frac{N}{(1 + 1/m)} \\
 d &= 0.
 \end{aligned} \tag{26}$$

The roots of equation (24) are  $D = 0$  and

$$D = \frac{(N - 2 - 1/m)}{N} \pm \frac{2\sqrt{1 + 1/m}}{N} \cos \alpha \tag{27}$$

The root  $D = 0$  obviously satisfies the stability requirement, and so only the root given by equation (27) must be checked.

$$-1 \leq \frac{(N - 2 - 1/m)}{N} \pm \frac{2\sqrt{1 + 1/m}}{N} \cos \alpha \leq 1. \tag{28}$$

Cosine  $\alpha$  may take on all values between -1 and +1 for all real values of  $\alpha$ . The right inequality is satisfied for all possible values of  $N$  and  $m$  with  $\alpha$  taking on all possible values. The left inequality is satisfied for all values of  $m$  and all  $N > 2.15$  for all possible values of  $\alpha$ . Since  $N = 6.7$  stability is assured.

The boundary conditions satisfy the stability theorem boundary since  $w$  and  $y$  are both zero,  $u(n)$  corresponds to the experimentally determined function of time,  $f(t)$ , and  $v(n)$  correspond to the function of time,  $g(t)$ , developed in Appendix B. The initial condition also satisfies the theorem since  $d = 0$  and since steady state was arbitrarily selected at time corresponding to  $n = 0$ .

## APPENJIX D

### THE FORTRAN PROGRAM

The FORTRAN program for the solution of finite difference equation (14) and the boundary and initial conditions of equation (11) is given below.

```

C  CYLINDER TRANSIENT HEAT TRANSFER OF AIR BLOWING REACTOR
      XEQ
      CARDS COLUMN
      SYMBOL TABLE
      DIMENSION T(7,350)
7  FORMAT(I6,7F9.2)
8  FORMAT(12F6.1)
9  FORMAT(I6,2F6.1)
4  READ INPUT TAPE 5,8,1 B,TC,TD,TE,TF,TG,TH,(T(7,N),N=2,6)
3  READ INPUT TAPE 5,9,JY,T(1,1),T(7,1)
      DO 40 M=2,6
      CM=M
      XY = LOGF((6.0+CM)/7.0)
40  T(M,1)=T(1,1)-(T(1,1)-T(7,1))*XY/0.619
      DO 1 N=12,JY,12
1  READ INPUT TAPE 5,8,T(1,N-11),T(1,N-10),T(1,N-9),T(1,N-8),T(1,N-7),
      T(1,N-6),T(1,N-5),T(1,N-4),T(1,N-3),T(1,N-2),T(1,N-1),T(1,N)
      DO 2 N=7,JY
      IF (N-40) 10,10,11
10  RN=N
      TA=TB + RN*(TC-TB)/40.0
      GO TO 22
11  IF (N-80) 12,13,13
12  NR=N-40
      RN=NR
      TA=TC + RN*(TD-TC)/40.0
      GO TO 22
13  IF (N-120)14,15,15
14  NR=N-80
      RN =NR
      TA = ID + RN*(TE-TD)/40.0
      GO TO 22

```

```

15 IF (N-160) 16,17,17
16 NR=N-120
   RN=NR
   TA = TE + RN*(TF-TE)/40.0
   GO TO 22
17 IF (N-200) 18,19,19
18 NR= N-160
   RN=NR
   TA=TF + RN*(TG-TF)/40.0
   GO TO 22
19 IF (N-260) 20,21,21
20 NR=N-200
   RN=NR
   TA = TG + RN*(TH-TG)/60.0
   GO TO 22
21 TA=TH
22 CONTINUE
   2 T(7,N)=0.0382*(T(1,N-6)-TA)+TA
   DO 6 N=2,JY
   DO 5 M=2,6
   CM=M
   A=1.0/(6.0+CM)
5 T(M,N)=((1.0+A)*T(M+1,N-1)+(4.7-A)*T(M,N-1)+T(M-1,N-1))/6.7
6 WRITE OUTPUT TAPE 6,7,N,(T(M,N),M=1,7)
   GO TO 4
   END(0,0,0,1,0,1,0,0,0,0,0,0,0,0,0,0)

```

## APPENDIX E

## CALIBRATIONS

TABLE 14

CHECK OF CALCULATIONS FROM VALUES OBTAINED WITH HEATER

Time, min.	Voltage, volts	Current, amps.	Heat Liberated by Heater, BTU	Calculated Heat Liberated, BTU	Per Cent Difference
7.1	230	11.35	1052	1007	-4.28
4.2	230	11.30	629	631	0.32
4.2	230	11.60	689	646	3.66

TABLE 15

REACTOR HEAT LOSS VALUES

535 - 550 °F.		460 - 475 °F.	
Run Number	Heat Lost, BTU/min.	Run Number	Heat Lost, BTU/min.
R-63-4	11.46	R-63-2	10.7
R-63-4	11.14	R-63-2	10.0
R-63-4	11.18	R-63-2	10.5
R-63-4	11.47	R-63-2	10.5
R-63-4	11.01	R-63-5	11.2
R-63-4	9.92	R-63-5	10.6
R-63-4	10.13	R-63-5	10.8
R-63-6	11.76	R-63-5	10.4
R-63-6	11.42	R-63-5	10.8
R-63-6	10.32		
R-63-8	13.11		
R-63-8	12.70		
R-63-8	12.85		
R-63-8	13.02		
R-63-8	12.51		
R-63-8	12.18		
Mean	11.64	Mean	10.61

The Beckman oxygen analyzer was calibrated after every air blowing run by recording its reading with pure, dry air. The results are tabulated in Table 16.

TABLE 16

## OXYGEN ANALYZER READINGS WITH PURE, DRY AIR

Date	Analyzer Reading	Date	Analyzer Reading
2-20-63	20.7	5-4-63	20.5
2-22-63	20.9	10-4-63	20.9
3-28-63	20.7	10-7-63	20.8
3-19-63	20.6	10-9-63	20.4
3-25-63	20.9	10-11-63	20.6
3-29-63	20.8	10-14-63	20.6
4-2-63	20.4	10-16-63	20.6
4-15-63	20.7	10-18-63	20.6
4-30-63	20.8	10-24-63	20.6
		11-8-63	20.6

The calibration curve for the exit flowmeter, which was calibrated against the factory calibrated inlet flowmeter, is shown as Figure 13.

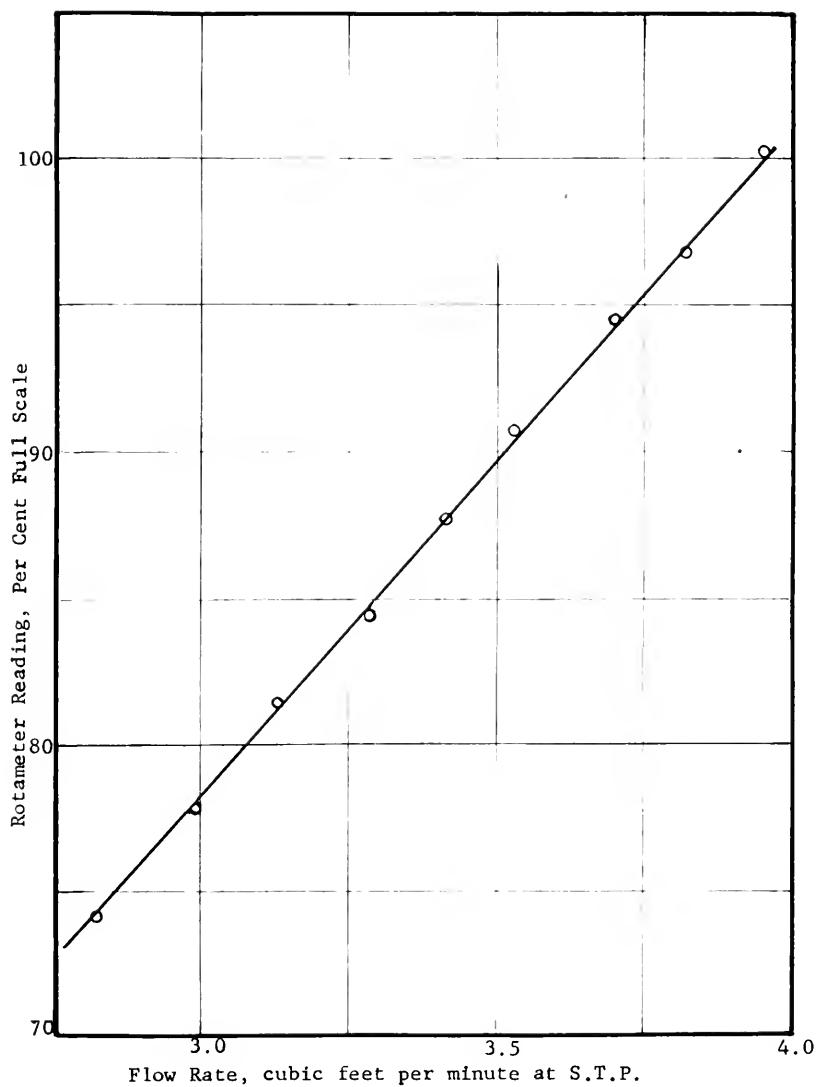


Figure 13. Exit Flowmeter Calibration Curve

## APPENDIX F

### CALCULATION OF HEATS OF REACTION

#### Procedure

The heat of reaction can be calculated from the heats of formation of reaction products and reactants by equation (29).

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \quad (29)$$

where

$$\Delta H_f = \text{Heat of formation, kcal. gm. mole}^{-1}$$

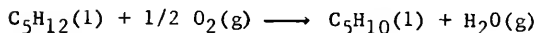
The reactions that have been proposed to occur in processing asphalt involve complicated molecules of unknown structure. To calculate the heat of reaction of the proposed reactions, it is necessary to approximate these structures by known compounds with experimentally measured heats of formation. Applying the principle that the heat of formation of a chemical bond is approximately constant and independent of the remaining structure of the molecule, the heat of reaction of the proposed reaction can be approximated by calculating the heat of reaction for the same reaction in which the products and reactants are relatively simple compounds. The heats of formation of the approximating compounds are available in reference works of thermodynamic properties (88, 79, 43, 5). It was also necessary to assume that the heat capacities of the reacting

species were independent of temperature. For the liquid phase this is not an unreasonable assumption.

### Air Blowing Reaction

The heats of reaction of the air blowing reactions proposed in Table 9 are as follows:

#### Dehydrogenation of Aliphatic Bond to Form an Olefin

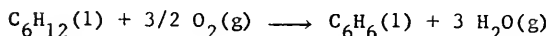


$$\Delta H = \Delta H_f(\text{C}_5\text{H}_{10}) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_5\text{H}_{12}) - 1/2 \Delta H_f(\text{O}_2)$$

$$\Delta H = (-11.16) + (-57.8) - (-41.40) - 1/2(0) = -27.6$$

$$\Delta H = -55.2 \text{ kcal./gm. mole O}_2$$

#### Aromatization of Naphthenic Ring to Aromatic Ring

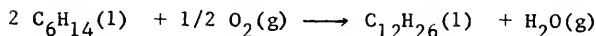


$$\Delta H = \Delta H_f(\text{C}_6\text{H}_6) + 3 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_{12}) - 3/2 \Delta H_f(\text{O}_2)$$

$$\Delta H = (11.72) + 3(-57.8) - (-37.3) - 3/2(0) = -124.4$$

$$\Delta H = -83.0 \text{ kcal./gm. mole O}_2$$

#### Direct Carbon-Carbon Bond Formation



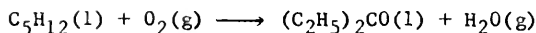
$$\Delta H = \Delta H_f(\text{C}_{12}\text{H}_{26}) + \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\text{C}_6\text{H}_{14}) - 1/2 \Delta H_f(\text{O}_2)$$

$$\Delta H = (184.16) + (-57.8) - 2(-47.52) - 1/2(0) = -46.94$$

$$\Delta H = -93.9 \text{ kcal./gm. mole O}_2$$

Formation of Oxygen Containing Functional Groups

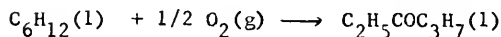
Ketone on side chain



$$\Delta H = \Delta H_f(\text{C}_2\text{H}_5\text{COC}_2\text{H}_5) + \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_5\text{H}_{12}) - \Delta H_f(\text{O}_2)$$

$$\Delta H = (-73.8) + (-57.8) - (-41.4) - (0) = 87.9 \text{ kcal./gm. mole O}_2$$

Ketone with naphthenic ring rupture

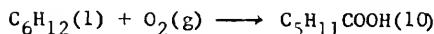


$$\Delta H = \Delta H_f(\text{C}_2\text{H}_5\text{COC}_3\text{H}_7) - \Delta H_f(\text{C}_6\text{H}_{12}) - 1/2 \Delta H_f(\text{O}_2)$$

$$\Delta H = (-79.96) - (37.34) - 1/2(0) = -42.62$$

$$\Delta H = 95.2 \text{ kcal./gm. mole O}_2$$

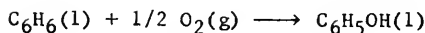
Carboxylic acid



$$\Delta H = \Delta H_f(\text{C}_5\text{H}_{11}\text{COOH}) - \Delta H_f(\text{C}_6\text{H}_{12}) - \Delta H_f(\text{O}_2)$$

$$\Delta H = (-140.08) - (-37.34) = -102.7 \text{ kcal./gm. mole O}_2$$

Hydroxyl group

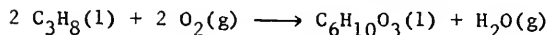


$$\Delta H = \Delta H_f(\text{C}_6\text{H}_5\text{OH}) - \Delta H_f(\text{C}_6\text{H}_6) - 1/2 \Delta H_f(\text{O}_2)$$

$$\Delta H = (-37.8) - (11.72) - 1/2(0) = -49.52$$

$$\Delta H = -99.0 \text{ kcal./gm. mole O}_2$$

Anhydride

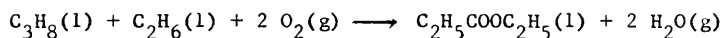


$$\Delta H = \Delta H_f(C_6H_{10}O_3) + \Delta H_f(H_2O) - 2 \Delta H_f(C_3H_8) - 2 \Delta H_f(O_2)$$

$$\Delta H = (-161.3) + (-57.8) - 2(-28.8) - 2(0) = -171.4$$

$$\Delta H = -85.7 \text{ kcal./gm. mole } O_2$$

#### Ester

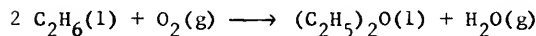


$$\Delta H = \Delta H_f(C_2H_5COOC_2H_5) + 2 \Delta H_f(H_2O) - \Delta H_f(C_3H_8) - \Delta H_f(C_2H_6) - 2 \Delta H_f(O_2)$$

$$\Delta H = (-122.2) + 2(-57.8) - (-28.4) - (-22.9) - 2(0) = -186.5$$

$$\Delta H = -93.2 \text{ kcal./gm. mole } O_2$$

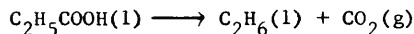
#### Ether



$$\Delta H = \Delta H_f(C_2H_5OC_2H_5) + \Delta H_f(H_2O) - 2 \Delta H_f(C_2H_6) - \Delta H_f(O_2)$$

$$\Delta H = (-65.2) + (-57.8) - 2(-22.9) - (0) = -77.2 \text{ kcal./gm. mole } O_2$$

#### Decarboxylation



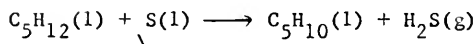
$$\Delta H = \Delta H_f(C_2H_6) + \Delta H_f(CO_2) - \Delta H_f(C_2H_5COOH)$$

$$\Delta H = (-22.9) + (-94.0) - (-121.7) = 4.8 \text{ kcal./gm. mole } CO_2$$

#### Sulphurization Reaction

The heats of reaction of the sulphurization reactions proposed in Table 12 are as follows:

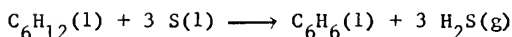
Dehydrogenation of Aliphatic Bond to Olefinic Double Bond



$$\Delta H = \Delta H_f(\text{C}_5\text{H}_{10}) + \Delta H_f(\text{H}_2\text{S}) - \Delta H_f(\text{C}_5\text{H}_{12}) - \Delta H_f(\text{S})$$

$$\Delta H = (-11.16) + (4.77) - (-41.40) - (0.67) = 24.8 \text{ kcal./gm. mole S}$$

Aromatization of Naphthenic Ring to Aromatic Ring

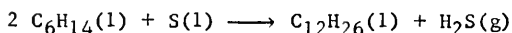


$$\Delta H = \Delta H_f(\text{C}_6\text{H}_6) + 3 \Delta H_f(\text{H}_2\text{S}) - \Delta H_f(\text{C}_6\text{H}_{12}) - 3 \Delta H_f(\text{S})$$

$$\Delta H = (11.72) + 3(-4.77) - (-37.34) - 3(0.67) = 32.7$$

$$\Delta H = 10.9 \text{ kcal./gm. mole S}$$

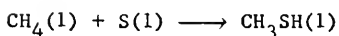
Direct Carbon-Carbon Bond Formation



$$\Delta H = \Delta H_f(\text{C}_{12}\text{H}_{26}) + \Delta H_f(\text{H}_2\text{S}) - 2 \Delta H_f(\text{C}_6\text{H}_{14}) - \Delta H_f(\text{S})$$

$$\Delta H = (-84.16) + (-4.77) - 2(-47.52) - (0.67) = 6.43 \text{ kcal./gm. mole S}$$

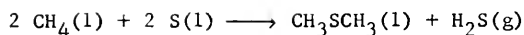
Thiol Formation



$$\Delta H = \Delta H_f(\text{CH}_3\text{SH}) - \Delta H_f(\text{CH}_4) - \Delta H_f(\text{S})$$

$$\Delta H = (-8.84) - (-19.9) - (0.67) = 10.4 \text{ kcal./gm. mole S}$$

### Sulphide Formation

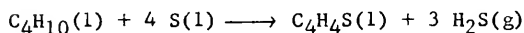


$$\Delta H = \Delta H_f(\text{CH}_3\text{SCH}_3) + \Delta H_f(\text{H}_2\text{S}) - 2 \Delta H_f(\text{CH}_4) - 2 \Delta H_f(\text{S})$$

$$\Delta H = (-13.6) + (-4.77) - 2(-19.94) - 2(0.67) = 20.2$$

$$\Delta H = 10.1 \text{ kcal./gm. mole S}$$

### Closure of Aliphatic Chain to Thiophene Type Ring



$$\Delta H = \Delta H_f(\text{C}_4\text{H}_4\text{S}) + 3 \Delta H_f(\text{H}_2\text{S}) - \Delta H_f(\text{C}_4\text{H}_{10}) - 4 \Delta H_f(\text{S})$$

$$\Delta H = (86.9) + 3(-4.77) - (-34.5) - 4(0.67) = 103.5$$

$$\Delta H = 25.9 \text{ kcal./gm. mole S}$$

### Dehydrogenation Followed by Sulphide Linkage Alpha to Double Bond

$$\Delta H = \Delta H_f(\text{two double bonds}) + \Delta H_f(\text{one sulphide bond})$$

$$\Delta H = 2(24.8) + 2(10.1) = 69.8$$

$$\Delta H = 17.4 \text{ kcal./gm. mole S}$$

### Dimerization Reactions of Alkyl Aromatics

Aliphatic linkage (same as C-C bond formation)

$$\Delta H = 6.4 \text{ kcal./gm. mole S}$$

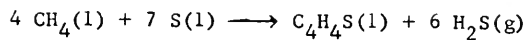
Olefinic linkage

$$\Delta H = \Delta H_f(\text{aliphatic C-C bond}) + \Delta H_f(\text{double bond})$$

$$\Delta H = (6.4) + (24.8) = 31.2$$

$$\Delta H = 15.6 \text{ kcal./gm. mole S}$$

Thiophene type linkage



$$\Delta H = \Delta H_f(\text{C}_4\text{H}_4\text{S}) + 6 \Delta H_f(\text{H}_2\text{S}) - 4 \Delta H_f(\text{CH}_4) - 7 \Delta H_f(\text{S})$$

$$\Delta H = (86.9) + 6(-4.77) - 44(-19.94) - 7(0.67) = 133.4$$

$$\Delta H = 19.1 \text{ kcal./gm. mole S}$$

## APPENDIX G

### SAMPLE CALCULATIONS

#### Air Blowing

As a sample calculation of the heat of reaction of air blowing asphalt, the calculations made to determine the heat of reaction for asphalt S-62-3 over the temperature range 535 to 550 °F. and the softening point range 100 to 130 °F. are illustrated here. The experimental data taken during Run R-63-4 over the incremental range of 370 to 380 minutes are given in Table 17.

The inlet flowmeter was calibrated to read in cubic feet of air per minute at a temperature of 70 °F. and a pressure of 14.7 pounds per square inch. The rate of flow in pounds per minute is given by

$$F_a = I \frac{29}{359} \sqrt{\frac{P}{14.7} \frac{530}{(T_{am} + 460)}} \quad (30)$$

where

$I$  = Flowmeter reading,  $\text{ft.}^3 \text{ min.}^{-1}$  at standard temperature and pressure

$P$  = Line pressure, psia.

The conversion factor 29/359 converts from standard cubic feet of air to pounds of air. The correction term for pressure

TABLE 17

EXCERPT FROM EXPERIMENTAL DATA, RUN R-63-4

Time, min.	Inlet Flow, cu. ft./ min.	Inlet Temperature, ° F.	Reactor Temperature, ° F.	Reactor Pressure, psig.	Exit Flow, Per Cent Scale	Oxygen Concentration, Per Cent	Ambient Air Temperature, ° F.
370	3.40	539	534.0	5.3	94.8	15.2	83
375	3.49	547	541.8	5.5	95.0	14.8	83
380	3.60	530	549.7	5.5	97.3	14.6	83

and temperature is necessary since the displacement of a flowmeter float is proportional to the square root of the density of the fluid (11).

The input and output terms are evaluated by equation (6).

$$H_a - H_o = -F_a C_a (T_{as} - T_a) \Delta t. \quad (6)$$

The numerical evaluation of this equation is shown in Table 18.

TABLE 18

## EVALUATION OF INPUT AND OUTPUT TERMS

Time, min.	$(T_{as} - T_a)_{avg},$ °F.	$F_a C_a (T_{as} - T_a)_{avg} \Delta t,$ BTU
370 - 375	0	0
375 - 380	7	2.9

The value of the factor  $(T_{as} - T_a)_{avg}$  is taken to be an average value of the 5-minute time interval.

$$(T_{as} - T_a)_{avg} = \frac{(T_{as} - T_a)_t + (T_{as} - T_a)_{t+\Delta t}}{2} \quad (31)$$

The accumulation of energy in asphalt and reactor is calculated directly from equations (7) and (8) respectively.

$$A_{as} = M_{as} C_{as} (T_2 - T_1) \quad (7)$$

$$A_{as} = (42.8)(0.40)(549.7 - 534.0) = 268 \text{ BTU}$$

$$A_r = M_r C_r (T_2 - T_1) \quad (8)$$

$$A_r = (137)(0.117)(549.7 - 534.0) = 251 \text{ BTU}$$

To calculate the accumulation of energy in the insulation, the values of  $T_2(r)$  and  $T_1(r)$  are read from the computer solution of equation (11). These values appear in Table 19.

TABLE 19

## TEMPERATURE AS A FUNCTION OF RADIUS

Radius, r, inches	Temperature at Time = 370 min., $T_1(r)$ , °F.	Temperature at Time = 380 min., $T_2(r)$ , °F.	Temperature Difference, $[T_2(r) - T_1(r)]$ , °F.
7	534.0	549.7	15.7
8	442.2	443.7	1.5
9	361.8	361.3	-0.5
10	287.4	287.2	-0.2
11	219.1	219.0	-0.1
12	156.4	156.2	-0.2
13	97.9	97.6	-0.3

With  $T_1(r)$  and  $T_2(r)$  now evaluated as functions of  $r$ , it is now possible to numerically evaluate the first integral of equation (9).

$$\int_{R_{\alpha}}^{R_{\beta}} \left[ T_2(r) - T_1(r) \right] r \, dr.$$

The value of  $\left[ T_2(r) - T_1(r) \right]$  over the incremental time interval from 370 to 380 minutes is taken to be the average value, which is defined by equation (32).

$$\left[ T_2(r) - T_1(r) \right]_{\text{avg}} = \frac{\left[ T_2(r) - T_1(r) \right]_t + \left[ T_2(r) - T_1(r) \right]_{t+\Delta t}}{2} \quad (32)$$

The numerical integration from  $R_{\alpha} = 7$  inches to  $R_{\beta} = 13$  inches in increments of 1 inch is shown in Table 20.

TABLE 20

## NUMERICAL INTEGRATION

Incremental Radius, inches	Average Radius, r, inches	$\left[ T_2(r)_{o_F} - T_1(r) \right]_{\text{avg}}$	$r \left[ T_2(r) - T_1(r) \right]$
7 - 8	7.5	8.6	64.5
8 - 9	8.5	0.5	4.2
9 - 10	9.5	-0.35	-3.3
10 - 11	10.5	-0.15	-1.6
11 - 12	11.5	-0.15	-1.7
12 - 13	12.5	-0.25	-3.1
			59.0

$$\int_7^{13} [T_2(r) - T_1(r)] r \, dr = 59.0 \text{ in.}^2 \text{ } ^\circ\text{F.}$$

$$2 \pi h C_i \rho \int_7^{13} [T_2(r) - T_1(r)] r \, dr = \frac{(2)(\pi)(20)(0.28)(11)(59.0)}{(12)^3}$$

$$= 13.2 \text{ BTU}$$

The accumulation of energy in the insulation on the ends of the reactor is assumed to be proportional to the accumulation of energy in the insulation on the sides of the reactor with the ratio of end heat transfer area to side heat transfer area taken as the constant of proportionality.

$$\frac{\text{End Area}}{\text{Side Area}} = \frac{2 \pi R_\alpha^2}{2 \pi R_\alpha h} = \frac{R_\alpha}{h} = \frac{7}{20}.$$

$$2 \pi R_\alpha^2 C_i \rho \int_0^6 [T_2(x) - T_1(x)] \, dx = (13.2) \frac{7}{20} = 4.6$$

$$A_i = 13.2 + 4.6 = 17.8 \text{ BTU.}$$

The heat losses are calculated from equation (15).

$$\begin{aligned} L &= L' \Delta t \\ L &= (11.64)(10) = 116.4 \text{ BTU} \end{aligned} \tag{15}$$

All of the individual terms in equation (2) have now been evaluated but since all values of the heat of reaction were calculated for liquid products, the heat of vaporization of the small quantity of material leaving the system as vapor must be considered and added to the value of Q.

$$V = \Delta H_v W \quad (33)$$

where

$W$  = Quantity of material evaporated, lb.

$\Delta H_v$  = Heat of vaporization, BTU lb.<sup>-1</sup>

$V$  = Heat required for vaporization of  $W$  lbs., BTU

Nelson (76) gives the heat of vaporization of hydrocarbons with a specific gravity of above 0.90, that of the precipitated oils, to be about 100 BTU per pound.

$$V = (100)(0.07) = 7 \text{ BTU}$$

The amount of heat liberated during this 10-minute increment can be calculated by summing all terms.

$$Q = 268 + 251 + 18 - (-3) + 116 + 7 = 663 \text{ BTU}$$

The quantity of oxygen consumed can be obtained by numerical integration of equation (16), but with low oxygen consumption the inlet and exit flow rates are approximately equal and small errors due to apparatus leaks or in the flowmeter readings would be magnified by subtraction. A less rigorous but experimentally more accurate value is obtained by equation (34)

$$G = F_o(0.209 - Y_o)(1 - 0.04) \Delta t / (29) \quad (34)$$

The factor  $(1 - 0.04)$  is required because the water vapor that goes through the flowmeter with the exit gas is removed prior to entering the oxygen analyzer.

$$\begin{aligned} G &= (0.304)(0.209 - 0.148)(1 - 0.04)(10)/29 \\ &= 6.13 \times 10^{-3} \text{ lb. moles} \end{aligned}$$

TABLE 21

EXCERPT FROM EXPERIMENTAL DATA, RUN R-63-25

Time, min.	Inlet N <sub>2</sub> Flow, cu. ft./min.	Inlet Pressure psig.	Inlet Temperature, ° F.	Reactor Temperature, ° F.	Ambient Air Temperature, ° F.
305	0	-	-	561.6	92
310	0	-	-	552.8	92
315	0	-	-	545.1	92
320	0	-	-	538.0	92
325	0	-	-	532.5	92
330	0	-	-	527.6	92
335	0	-	-	522.5	92
340	0	-	-	517.0	92
345	0	-	-	511.0	92
350	0	-	-	504.5	92
355	0	-	-	500.0	92
360	0	-	-	494.0	92
365	0	-	-	489.0	92
370	0	-	-	485.9	92
375	0	-	-	483.0	92
380	0.9	0.1	90	480.2	92
385	0.9	0.1	90	479.2	92
390	0.9	0.1	90	477.5	92

Quantity of sulphur added = 1565 grams

The heat of reaction is then found easily from equation (17).

$$\Delta H = \frac{-Q \times 10^{-3}}{1.8 \text{ G}} \quad (17)$$

$$\Delta H = -(603)10^{-3}/(1.8)(6.13 \times 10^{-3}) = -60.1 \text{ kcal./gm.mole}$$

### Sulphurization

As a sample calculation of the heat of reaction of sulphurizing asphalt, the calculations made to determine one value of the heat of reaction for asphalt S-63-3 are illustrated here. The experimental data taken during Run R-63-25 over the incremental time period of 305 to 390 minutes are given in Table 21.

The evaluation of input and output terms by equation (6) is shown in Table 22.

TABLE 22

### EVALUATION OF INPUT AND OUTPUT TERMS

Time, min.	$(T_{as} - T_a)_{avg},$ $^{\circ}F.$	$F_a C_a (T_{as} - T_a)_{avg}$ BTU	$\Delta t,$
305 - 380	--	0	
380 - 385	390	36.4	
385 - 390	388	36.3	
TOTAL		72.7	

The accumulation of energy in asphalt and reactor is calculated from equations (7) and (8) respectively.

$$A_a = (41)(0.40)(477.5 - 561.6) = -1380 \text{ BTU}$$

$$A_r = (137)(0.117)(477.5 - 561.6) = -1356 \text{ BTU}$$

The accumulation of energy in the insulation is calculated by the reading of values of  $T_2(r)$  and  $T_1(r)$  from the computer solution of equation (11) and the numerical integration of equation (9).

TABLE 23

TEMPERATURE AS A FUNCTION OF RADIUS

Radius, r, inches	$T_1(r)$ , °F.	$T_2(r)$ , °F.	$[T_2(r) - T_1(r)]$ , °F.
7	561.6	477.5	-84.1
8	437.5	414.0	-23.5
9	345.9	347.7	1.8
10	276.1	281.5	5.4
11	215.0	218.9	3.9
12	159.1	161.1	2.0
13	107.7	107.4	- 0.3

The numerical integration from  $R_{\alpha} = 7$  inches to  $R_{\beta} = 13$  inches in increments of 1 inch is shown in Table 24.

TABLE 24

## NUMERICAL INTEGRATION

Incremental Radius, inches	Average Radius, r, inches	$\left[ T_2(r) - T_1(r) \right]_{\text{avg}}$ ° F.	$r \left[ T_2(r) - T_1(r) \right]$ inches ° F.
7 - 8	7.5	- 53.8	- 404
8 - 9	8.5	- 10.8	- 92
9 - 10	9.5	3.6	34
10 - 11	10.5	4.6	48
11 - 12	11.5	3.0	33
12 - 13	12.5	0.8	10
			- 371

$$2 \pi h C_i \rho \int_7^{13} \left[ T_2(r) - T_1(r) \right] r \, dr = \frac{(2)(\pi)(20)(0.28)(11)(-371)}{12^3}$$

$$= -82.9$$

The ratio of heat transfer areas is used to obtain the accumulation of energy in the ends of the reactor.

$$A_i = -82.9 - (82.9) \frac{7}{20} = -111.9 \text{ BTU}$$

The heat losses are calculated from equation (15).

$$L = (11.2)(85) = 953 \text{ BTU}$$

All of the individual terms in equation (2) have now been evaluated but since the molten sulphur was added at its freezing point, 245 °F., which was lower than the temperature of the system, this must be considered in the heat balance.

$$Z = 32 G C_s (T_{as} - T_s) \quad (35)$$

where

$Z$  = Heat effect of sulphur addition, BTU

$C_s$  = Heat capacity of sulphur, BTU lb.<sup>-1</sup> °F.<sup>-1</sup>

$T_s$  = Temperature of sulphur, °F.

A mean value of  $T_{as}$  is taken for this calculation.

$$Z = (1565)(0.220)(510 - 245)/(454) = 204 \text{ BTU}$$

The value of  $Q$  can now be obtained by summing all terms.

$$Q = -1380 - 1356 - 111 + 73 + 952 + 204 = -1619 \text{ BTU}$$

The heat of reaction can now be obtained from equation (17).

$$\begin{aligned} \Delta H &= - \frac{Q \times 10^{-3}}{1.8 G} = -(-1619)(10^{-3})(454)(32)/(1565)(1.8) \\ &= 8.33 \text{ kcal./gm. mole} \end{aligned}$$

## STATISTICAL DATA

TABLE 25

## SULPHURIZATION STATISTICAL DATA

	S-62-2	S-62-3	S-63-3	Total
Replications	4	5	6	15
Sum	48.8	40.8	53.8	143.4
Mean	12.2	8.16	8.96666	
Sum of Squares	602.90	340.86	485.30	1,429.06
$(\text{Sum})^2/\text{Rep.}$	595.36	332.928	482.40666	1,410.69466
Difference	7.54	7.932	2.89333	18.36533

TABLE 26

## CATALYTIC AIR BLOWING STATISTICAL DATA

	No Catalyst	P <sub>2</sub> O <sub>5</sub>	AlCl <sub>3</sub>	Total
Replications	4	2	2	8
Sum	247.7	123.9	142.1	513.7
Mean	61.925	61.95	71.05	
Sum of Squares	15,348.47	7,680.41	10,096.21	33,125.09
(Sum) <sup>2</sup> /Rep.	15,338.8225	7,675.605	10,096.205	33,110.6325
Difference	9.6475	4.805	0.005	14.4575

TABLE 27

## CATALYTIC AIR BLOWING ANALYSIS OF VARIANCE

Source	Degrees of Freedom	Sum of Squares	Mean Square
Among	2	124.67125	62.33562
Within	5	14.4575	2.8915
Total	7	139.12875	

TABLE 28

## AIR BLOWING FACTORIAL DESIGN DATA

Asphalt-A	Temperature-C	Softening Point-B 100-130 B <sub>1</sub>	130-180 B <sub>2</sub>	180-250 B <sub>3</sub>	Total B <sub>1</sub> +B <sub>2</sub> +B <sub>3</sub>
	460-475 C <sub>1</sub>	144.4	142.5	145.9	432.8 A <sub>1</sub> C <sub>1</sub>
S-62-2	535-550 C <sub>2</sub>	134.2	130.4	129.5	394.1 A <sub>1</sub> C <sub>2</sub>
A <sub>1</sub>	Total C <sub>1</sub> +C <sub>2</sub>	278.6 A <sub>1</sub> B <sub>1</sub>	272.9 A <sub>1</sub> B <sub>2</sub>	275.4 A <sub>1</sub> B <sub>3</sub>	826.9 A <sub>1</sub>
	460-475 C <sub>1</sub>	127.2	127.3	122.5	377.0 A <sub>2</sub> C <sub>1</sub>
S-62-3	535-550 C <sub>2</sub>	120.3	123.3	123.9	367.5 A <sub>2</sub> C <sub>2</sub>
A <sub>2</sub>	Total C <sub>1</sub> +C <sub>2</sub>	247.5 A <sub>2</sub> B <sub>1</sub>	250.6 A <sub>2</sub> B <sub>2</sub>	246.4 A <sub>2</sub> B <sub>3</sub>	744.5 A <sub>2</sub>
	460-475 C <sub>1</sub>	136.3	138.6	142.1	417.0 A <sub>3</sub> C <sub>1</sub>
S-63-3	535-550 C <sub>2</sub>	135.5	138.6	136.3	410.4 A <sub>3</sub> C <sub>2</sub>
A <sub>3</sub>	Total C <sub>1</sub> +C <sub>2</sub>	271.8 A <sub>3</sub> B <sub>1</sub>	277.2 A <sub>3</sub> B <sub>2</sub>	278.4 A <sub>3</sub> B <sub>3</sub>	827.4 A <sub>3</sub>
Total	460-475 C <sub>1</sub>	407.9 B <sub>1</sub> C <sub>1</sub>	408.4 B <sub>2</sub> C <sub>1</sub>	410.5 B <sub>3</sub> C <sub>1</sub>	1226.8 C <sub>1</sub>
A <sub>1</sub> +A <sub>2</sub> +A <sub>3</sub>	535-550 C <sub>2</sub>	390.0 B <sub>1</sub> C <sub>2</sub>	392.3 B <sub>2</sub> C <sub>2</sub>	389.7 B <sub>3</sub> C <sub>2</sub>	1172.0 C <sub>2</sub>
	Total C <sub>1</sub> +C <sub>2</sub>	797.9 B <sub>1</sub>	800.7 B <sub>2</sub>	800.2 B <sub>3</sub>	2398.8
	Block 1	1199.7			
	Block 2	1199.1			

## APPENDIX I

## TABULATED DATA

TABLE 29

## AIR BLOWING DATA

Run Number	Asphalt	Softening Point ° F.	Temperature, ° F.	Heat Generated BTU	Oxygen lb. mole x 10 <sup>3</sup>	Heat of Reaction, kcal./ gm. mole
R-63-2	S-62-3	70-100	460-475	973	8.50	-63.6
R-63-2	S-62-3	70-100	460-475	1049	8.97	-65.0
R-63-2	S-62-3	70-100	460-475	986	8.28	-65.1
R-63-2	S-62-3	100-130	460-475	959	8.70	-61.3
R-63-2	S-62-3	100-130	460-475	1200	9.84	-67.8
R-63-2	S-62-3	130-180	460-475	1353	11.43	-65.7
R-63-2	S-62-3	130-180	460-475	1202	10.10	-66.1
R-63-2	S-62-3	180-250	460-475	2643	25.80	-57.0
R-63-3	S-62-2	100-130	460-475	2103	16.00	-73.2
R-63-3	S-62-2	130-180	460-475	2138	16.70	-71.0
R-63-3	S-62-2	180-250	460-475	357	2.60	-76.3
R-63-3	S-62-2	180-250	460-475	823	6.27	-73.0
R-63-3	S-62-2	180-250	460-475	343	2.62	-72.7
R-63-4	S-62-3	70-100	535-550	675	6.07	-61.8
R-63-4	S-62-3	70-100	535-550	668	5.94	-62.5
R-63-4	S-62-3	70-100	535-550	672	6.32	-59.0
R-63-4	S-62-3	70-100	535-550	693	6.32	-61.0
R-63-4	S-62-3	100-130	535-550	935	8.61	-60.3
R-63-4	S-62-3	130-180	535-550	854	7.89	-60.1
R-63-4	S-62-3	130-180	535-550	767	7.13	-59.8
R-63-4	S-62-3	180-250	535-550	766	6.84	-62.3
R-63-4	S-62-3	180-250	535-550	1287	12.50	-57.2
R-63-4	S-62-3	180-250	535-550	470	3.63	-71.9
R-63-5	S-62-3	70-100	460-475	1372	11.70	-65.2
R-63-5	S-62-3	70-100	460-475	1062	9.45	-62.5
R-63-5	S-62-3	70-100	460-475	988	9.25	-59.3
R-63-5	S-62-3	70-100	460-475	881	8.70	-56.4
R-63-5	S-62-3	100-130	460-475	993	8.69	-63.5
R-63-5	S-62-3	100-130	460-475	991	8.80	-62.6
R-63-5	S-62-3	130-180	460-475	715	6.40	-62.1
R-63-5	S-62-3	130-180	460-475	1537	13.92	-61.3

TABLE 29--Continued

Run Number	Asphalt	Softening Point ° F.	Temperature, ° F.	Heat Generated BTU	Oxygen lb. mole x 10 <sup>3</sup>	Heat of Reaction, kcal./ gm. mole
R-63-5	S-62-3	180-250	460-475	1740	14.57	-65.5
R-63-6	S-62-2	100-130	535-550	1105	9.69	-65.8
R-63-6	S-62-3	100-130	535-550	1100	8.43	-69.8
R-63-6	S-62-2	130-180	535-550	774	6.55	-65.7
R-63-6	S-62-2	130-180	535-550	1040	8.58	-67.3
R-63-6	S-62-2	130-180	535-550	1013	9.27	-60.7
R-63-6	S-62-2	180-250	535-550	1002	8.85	-62.9
R-63-7	S-62-2	100-130	460-475	737	6.25	-65.5
R-63-7	S-62-2	100-130	460-475	1805	13.01	-76.9
R-63-7	S-62-2	130-180	460-475	2728	21.20	-71.5
R-63-7	S-62-2	180-250	460-475	645	4.73	-75.7
R-63-7	S-62-2	180-250	460-475	500	3.91	-71.8
R-63-7	S-62-2	180-250	460-475	349	2.84	-68.3
R-63-8	S-62-3	70-100	535-550	1061	9.36	-62.9
R-63-8	S-62-3	70-100	535-550	747	6.75	-61.5
R-63-8	S-62-3	70-100	535-550	984	9.16	-59.6
R-63-8	S-62-3	100-130	535-550	718	6.68	-59.7
R-63-8	S-62-3	100-130	535-550	915	8.41	-60.5
R-63-8	S-62-3	130-180	535-550	877	7.86	-62.0
R-63-8	S-62-3	130-180	535-550	976	8.65	-62.8
R-63-8	S-62-3	130-180	535-550	863	7.35	-65.2
R-63-8	S-22-3	180-250	535-550	2712	26.10	-57.8
R-63-8	S-62-3	180-250	535-550	4332	38.50	-62.5
R-63-9	S-62-2	100-130	535-550	1648	13.80	-66.4
R-63-9	S-62-2	130-180	535-550	1562	13.20	-65.8
R-63-9	S-62-2	180-250	535-550	1235	10.78	-63.7
R-63-9	S-62-2	180-250	535-550	3543	28.30	-69.6
R-63-41	S-63-3	100-130	460-475	1270	10.31	-68.5
R-63-41	S-63-3	130-180	460-475	1450	11.30	-71.3
R-63-41	S-63-3	180-250	460-475	419	3.36	-69.3
R-63-42	S-63-3	100-130	535-550	1656	13.65	-67.4
R-63-42	S-63-3	130-180	535-550	1470	10.91	-75.8
R-63-42	S-63-3	130-180	535-550	1272	11.00	-64.3
R-63-42	S-63-3	180-250	535-550	2402	19.50	-68.5

TABLE 29--Continued

Run Number	Asphalt	Softening Point ° F.	Temperature, ° F.	Heat Generated BTU	Oxygen lb. mole x 10 <sup>3</sup>	Heat of Reaction, kcal./ gm. mole
R-63-43	S-63-3	100-130	460-475	1780	14.60	-67.8
R-63-43	S-63-3	130-180	460-475	535	4.25	-70.0
R-63-43	S-63-3	130-180	460-475	224	1.93	-64.5
R-63-43	S-63-3	180-250	460-475	123	0.94	-72.8
R-63-44	S-63-3	100-130	535-550	1747	14.24	-68.1
R-63-44	S-63-3	130-180	535-550	2607	21.08	-68.7
R-63-44	S-63-3	180-250	535-550	1932	15.99	-67.8

TABLE 30

## CATALYTIC AIR BLOWING DATA

Run Number	Catalyst	Heat Generated, BTU	Oxygen, lb. mole $\times 10^3$	Heat of Reaction kcal./gm. mole
R-63-49	$P_2O_5$ , 2%	7252	63.5	-63.5
R-63-50	$P_2O_5$ , 2%	5208	48.0	-60.4
R-63-56	$AlCl_3$ , 2%	6017	47.2	-71.0
R-63-62	$AlCl_3$ , 2%	6445	50.3	-71.1

TABLE 31

## SULPHURIZATION DATA

Run Number	Asphalt	Heat Generated, BTU	Sulphur, grams	Heat of Reaction, kcal./gm. mole
R-63-17	S-62-3	- 396	385.5	8.3
R-63-17	S-62-3	- 998	1223.4	6.6
R-63-19	S-62-3	-1204	1295.0	7.5
R-63-20	S-62-2	- 759	548.0	11.2
R-63-20	S-62-2	-1005	552.0	14.5
R-63-25	S-63-3	-1233	1156.0	8.6
R-63-25	S-63-3	-1662	1427.0	9.4
R-63-25	S-63-3	-1619	1565	8.3
R-63-27	S-63-3	- 612	558	8.8
R-63-28	S-63-3	-1341	1042	10.3
R-63-28	S-63-3	- 892	859	8.4
R-63-29	S-62-3	-1749	1344	10.4
R-63-29	S-62-3	-1115	1125	8.0
R-63-30	S-62-2	-1597	1077	12.0
R-63-30	S-62-2	-1413	1029	11.1

TABLE 32

## OXYGEN ANALYSES OF SAMPLES

Run Number	Asphalt, Catalyst	Temperature, ° F.	Softening Point, ° F.	Oxygen Reacted, lb. moles	Oxygen Concentra- tion, %	Oxygen in Asphalt, lb. moles $\times 10^3$	Per Cent Oxygen Retained
R-63-2	S-62-3	460-475	130	60.4	1.61	18.5	30.8
R-63-2	S-62-3	460-475	255	108.7	2.01	23.9	20.1
R-63-4	S-62-3	535-550	150	83.9	1.55	18.1	21.6
R-63-7	S-62-2	460-475	126	20.9	0.62	3.7	17.7
R-63-43	S-63-3	460-475	147	17.6	1.33	9.1	50.3
R-63-49	S-62-3	460-550	152	64.6	1.64	20.2	31.3
--	P <sub>2</sub> O <sub>5</sub>	--	--	--	0.52*	4.2*	6.5*
R-63-56	S-62-3	460-550	136	78.7	1.96	23.8	30.3
--	AlCl <sub>3</sub>	--	--	--	--	--	--

\*Excluding oxygen added in phosphorus pentoxide.

## NOMENCLATURE

A	= Accumulation of energy, BTU
a	= Constant in finite difference stability criterion
B	= Final boundary in finite difference stability criterion
b	= Constant in finite difference stability criterion
C	= Heat capacity, BTU lb. <sup>-1</sup> °F. <sup>-1</sup>
c	= Constant in finite difference stability criterion
D	= Root in finite difference stability criterion
d	= Constant in finite difference stability criterion
F	= Flow rate, lb. min. <sup>-1</sup>
f	= Boundary condition of equation (11)
G	= Reactant consumed, lb. moles
g	= Boundary condition of equation (11)
H	= Enthalpy, BTU
Δ H	= Heat of reaction, cal. gm. mole <sup>-1</sup>
h	= Height of reactor, in.
I	= Flowmeter reading, ft. <sup>3</sup> min. <sup>-1</sup>
k	= Thermal conductivity of insulation, BTU min. <sup>-1</sup> °F. <sup>-1</sup> in. <sup>-1</sup>
L	= Heat losses, BTU
L'	= Calibrated rate of heat loss, BTU min. <sup>-1</sup>
M	= Mass, lb.
m	= $r / \Delta r$
N	= $\rho C_i (\Delta r)^2 / k (\Delta t)$

- $P$  = Pressure, psia.  
 $p$  = Replications with standard in Dunnett's (23) test  
 $Q$  = Heat generated by reaction, BTU  
 $q$  = Replications with comparison in Dunnett's (23) test  
 $R$  = Radius, in.  
 $r$  = Distance from axis of cylinder to any point on radius, in.  
 $S$  = Heat transfer area, linear ft. of reactor  
 $s$  = Error mean square  
 $T$  = Temperature,  $^{\circ}\text{F}$ .  
 $t$  = Time, min.  
 $u$  = Function of time in finite difference stability criterion  
 $V$  = Heat leaving system due to vaporization, BTU  
 $v$  = Function of time in finite difference stability criterion  
 $W$  = Quantity of oils collected, lb.  
 $w$  = Constant in finite difference stability criterion  
 $x$  = Thickness of insulation on ends of reactor, in.  
 $Y$  = Oxygen concentration, mass fraction  
 $y$  = Constant in finite difference stability criterion  
 $Z$  = Heat effect of sulphur addition, BTU  
 $z$  = Distance measured along axis of cylinder, in.  
 $\alpha$  = Variable in finite difference stability criterion  
 $\delta$  = Dunnett's (23) difference  
 $\theta$  = Angle between  $r$  and  $x$ -axes, radians  
 $\lambda$  = Heat transfer coefficient,  $\text{BTU (linear ft.)}^{-1} \text{ } ^{\circ}\text{F.}^{-1} \text{ hr.}^{-1}$

- $U$  = Heat transfer coefficient,  $\text{BTU (linear ft.)}^{-1} \text{ } ^\circ\text{F.}^{-1} \text{ hr.}^{-1}$   
 $\rho$  = Density of insulation,  $\text{lb. in.}^{-3}$   
 $\gamma$  = Dunnett's (23)  $t$   
 $\psi$  = Rate of heat transfer,  $\text{BTU hr.}^{-1}$

# Subscripts

- $a$  = Inlet air  
 $am$  = Ambient air  
 $as$  = Asphalt  
 $d$  = Datum  
 $f$  = Formation  
 $i$  = Insulation  
 $m$  = Finite difference position  
 $n$  = Finite difference time  
 $o$  = Exit gas  
 $r$  = Reactor vessel  
 $s$  = Sulphur  
 $v$  = Vaporization  
 $\alpha$  = Inner radius of insulation (reactor radius)  
 $\beta$  = Outer radius of insulation  
 $1$  = time  $t$   
 $2$  = time +  $\Delta t$

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## BIOGRAPHICAL SKETCH

Douglas Bruce Smith was born June 23, 1936, at Galesburg, Illinois. In June, 1954, he was graduated from Manatee County High School, Bradenton, Florida. After graduation he entered the United States Coast Guard, in which he served for a period of three years and nine months. He entered the University of Florida in February, 1958 and received the degree of Bachelor of Chemical Engineering with High Honors in June, 1961 and the degree of Master of Science in Engineering in August, 1962. Since that time he has pursued his doctorate at the University of Florida as a National Science Foundation Cooperative Fellow.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 18, 1964

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